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JOURNAL
OF THE
INDIAN CHEMICAL SOCIETY

VOL. XXXV FEBRUARY, 1958 No. 2

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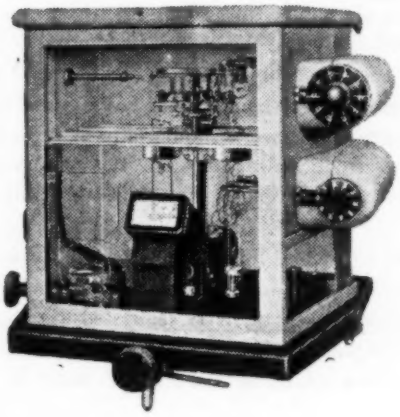

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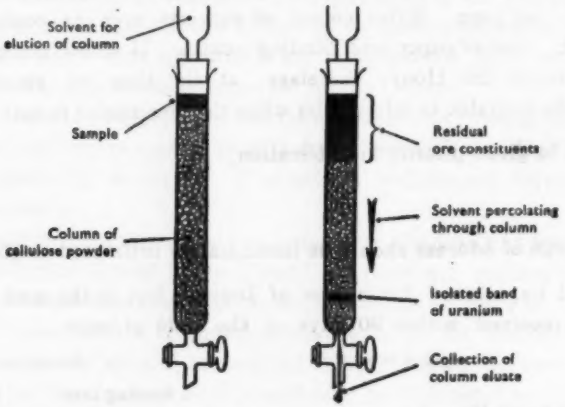

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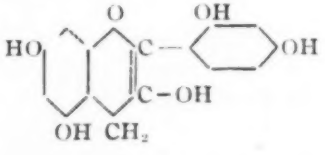
EXPERIMENTS ON THE SYNTHESIS OF CYANOMACLURIN AND RELATED SUBSTANCES. PART II*

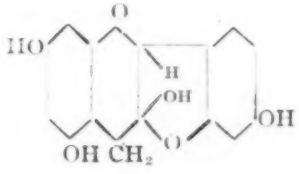
By R. B. Desai and J. N. Ray

6-Methoxycoumaranone has been condensed with salicylaldehyde, β-resorcylaldehyde, 2-hydroxy-4-methoxybenzaldehyde, 2-hydroxy-4 :6-dimethoxybenzaldehyde and 2-hydroxynaphthaldehyde in presence of piperidine to give the corresponding arylidene-coumaranones in good yields. Excepting 6-methoxy-2-(2 :4-dihydroxybenzylidene)-coumaranone, all these arylidene-coumaranones are reduced to the corresponding aryl derivatives. The aryl coumaranones have been cyclised by means of phosphorus pentoxide to the corresponding chromene derivatives.

Previous attempts at the synthesis of cyanomaclurin, notably by Bhalla and Ray (*J. Chem. Soc.*, 1933, 288) and Fonseca (*ibid.*, 1947, 1683), aimed at synthesising a structure (I) as assigned by Perkin (*ibid.*, 1905, **87**, 714) to cyanomaclurin. Since, however, the semi-acetal formula (II) for cyanomaclurin, as proposed by Appel and Robinson (*ibid.*, 1935, 752), seemed to be more plausible on available chemical and physical evidences, attempts have now been made to synthesise a substance corresponding to the semi-acetal structure.

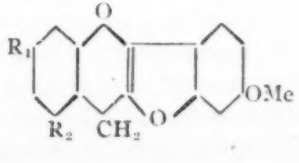


(I)

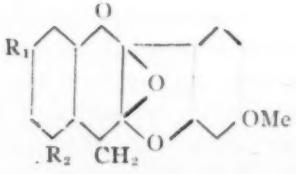


(II)

The initial step in one of the two schemes envisaged for this purpose was the preparation of the methiodide of a Mannich base from phloroglucinol or its methyl ether and its subsequent condensation with 6-methoxycoumaranone (cf. Robinson *et al.*, *J. Chem. Soc.*, 1937, 53 ; 1941, 589 ; Wilds and Shunk, *J. Amer. Chem. Soc.*, 1943, **65**, 469). The resulting tetracyclic condensation product (III), a benzofuranochromene derivative, on epoxidation with a per-acid could give an epoxide (IV), which on subsequent catalytic hydrogenation could furnish either (V) and/ or (VI). Thus :

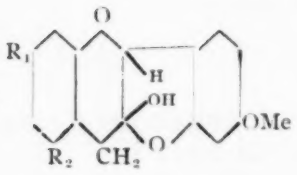


(III)

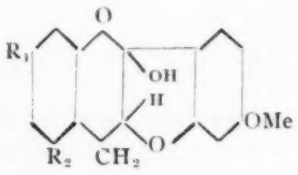


(IV)

*Part I—Bhalla and Ray, *J. Chem. Soc.*, 1933, 288.



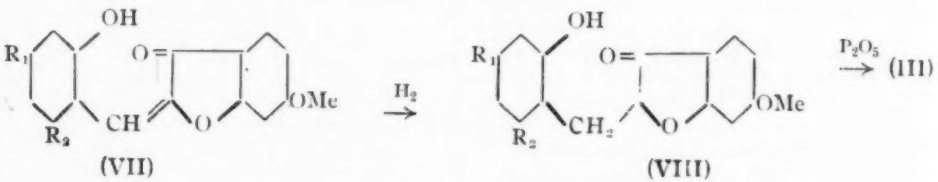
(V)



(VI)

However, the Mannich reaction with phloroglucinol or its methyl ether has been reported by De'Combe (*Compt. rend.*, 1933, **197**, 258) to give resinous products. This observation has been confirmed by the present authors. Therefore, attempts were made to prepare a Mannich base from 6-methoxycoumaranone which in the form of its methiodide was expected to condense with phloroglucinol to give (III). Despite numerous attempts 6-methoxycoumaranone failed to provide a definite compound in the Mannich reaction with dimethylamine and formaldehyde. This we attribute to its reacting in two tautomeric forms.

In the alternative route, which was then examined, the initial step consisted in the condensation of an appropriate *ortho*-hydroxybenzaldehyde with 6-methoxycoumaranone. The resulting condensation product (VII), an arylidene-coumaranone, could then be reduced catalytically and the reduction product, (VIII), cyclised according to standard methods, thus giving rise to a benzofuranochromene derivative (III), as comtemplated in the earlier scheme.



(VII) (VIII)

In order to explore the method, experiments were first carried out with salicylaldehyde. It was condensed with 6-methoxycoumaranone in presence of piperidine to give 6-methoxy-2-(2-hydroxybenzylidene)-coumaranone in excellent yield (cf. Auwers and Pohl, *Annalen*, 1914, **405**, 243 ; Shriner and Anderson, *J. Amer. Chem. Soc.*, 1938, **60**, 1415).

6-Methoxy-2-(2-hydroxybenzylidene)-coumaranone on catalytic hydrogenation with palladium gave 6-methoxy-2-(2-hydroxybenzyl)-coumaranone. The reduction product was cyclised by refluxing its solution in dry benzene with phosphorus pentoxide, when 2 : 3-(3′ : 2′ : 6′-methoxybenzofurano)-chromene was obtained in good yield. When this chromene was subjected to epoxidation with monoperphthalic acid in ether solution at 0°, only phthalic acid and a red coloured pasty product were obtained. The use of an inert atmosphere or application of a modified method (Chakravarty and Levine, *J. Amer. Chem. Soc.*, 1942, **64**, 2319) of epoxidation with perbenzoic acid gave similar results. With 30% hydrogen peroxide (Rohrman, Jones and Shonle, *ibid.*, 1944, **66**, 1854), the unchanged chromene was the only product isolated.

Similarly, β-resorcylaldehyde, 2-hydroxy-4-methoxybenzaldehyde, 2-hydroxy-4:6-dimethoxybenzaldehyde and 2-hydroxy-1-naphthaldehyde smoothly condensed with 6-methoxycoumaranone in presence of piperidine to give respectively 6-methoxy-2-(2:4-dihydroxybenzylidene)-, 6-methoxy-2-(2-hydroxy-4-methoxybenzylidene)-, 6-methoxy-2-(2-hydroxy-4:6-dimethoxybenzylidene)- and 6-methoxy-2-(2-hydroxy-1-naphthylidene)-coumaranones in good yields. Excepting 6-methoxy-2-(2:4-dihydroxybenzylidene)-coumaranone, all other arylidene-coumaranones could be reduced to the corresponding aryl-coumaranones. The reduction products, when cyclised, as described above, gave rise to the corresponding chromene derivatives.

EXPERIMENTAL

6-Methoxy-2-(2-hydroxybenzylidene)-coumaranone (VII: $R_1 = R_2 = H$).—6-Methoxycoumaranone (1 g.) and salicylaldehyde (0.8 g.) were dissolved in hot alcohol (10 c.c.) and then piperidine (1 c.c.) was added dropwise. The solution which became deep red in colour was left at room temperature overnight. It was then filtered from the separated yellow crystalline material which was recrystallised from acetic acid, m.p. 258-59° (decomp.), yield 1.6 g. (95%). (Found: C, 71.6; H, 4.4. $C_{16}H_{12}O_4$ requires C, 71.6; H, 4.5%). The *acetyl* derivative was crystallised from rectified spirit or ethyl acetate in pale yellow needles, m.p. 163-65°. (Found: C, 69.6; H, 5.1. $C_{18}H_{14}O_5$ requires C, 69.7; H, 4.5%).

6-Methoxy-2-(2-hydroxybenzyl)-coumaranone (VIII: $R_1 = R_2 = H$).—6-Methoxy-2-(2-hydroxybenzylidene)-coumaranone (1 g.) was dissolved in sufficient quantity of hot alcohol (*ca.* 300 c.c.) and the solution transferred to a hydrogenation bottle. Palladium chloride solution (1 c.c. of 1%) and a little purified charcoal were then added and the reduction carried out in a Parr hydrogenation apparatus. Within about one hour the solution became colorless. It was filtered and on removal of the solvent a colorless crystalline compound was obtained which was recrystallised from methyl alcohol in colorless needles, m.p. 145°, yield 0.6 g. (60%). (Found: C, 71.0; H, 5.5. $C_{16}H_{14}O_4$ requires C, 71.1; H, 5.2%).

2:3-(3′:2′:6′-Methoxybenzofurano)-chromene (III: $R_1 = R_2 = H$).—6-Methoxy-2-(2-hydroxybenzyl)-coumaranone (1 g.) was dissolved in hot dry benzene and P_2O_5 (*ca.* 2 g.) was added to the solution, which was refluxed on a water-bath for 2 hours, and then decanted off. On removal of benzene a colorless crystalline compound was obtained which was recrystallised from methyl alcohol in colorless needles, m.p. 108°, yield 0.5 g. (45-50%). (Found: C, 76.3; H, 5.1. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.8%).

6-Methoxy-2-(2:4-dihydroxybenzylidene)-coumaranone (VII: R_1 = OH; $R_2 = H$).—6-Methoxycoumaranone (1 g.) and β-resorcylaldehyde (1.38 g.) were dissolved in hot alcohol (10 c.c.) and to the hot solution pipiperidine (1 c.c.) was added dropwise. After 24 hours the crystalline solid, which had separated, was collected and recrystallised from alcohol or acetic acid, m.p. 244-46° (decomp.), yield 1.3 g. (45%). (Found: C, 67.4; H, 4.5. $C_{16}H_{12}O_5$ requires C, 67.6; H, 4.23%). The *acetyl* derivative was

crystallised from alcohol in colorless tiny needles, m.p. 159-61°. (Found : C, 64.9 ; H, 4.4. $C_{20}H_{16}O_7$ requires C, 65.2 ; H, 4.3%).

6-Methoxy-2-(2-hydroxy-4-methoxybenzylidene) - coumaranone (VII : R_1 = OMe ; R_2 = H) :—6-Methoxycoumaranone (1.64 g., 0.01 *M*) and 2-hydroxy-4-methoxybenzaldehyde (1.52 g., 0.01 *M*) were condensed as before. The product, an orange-coloured crystalline solid, was recrystallised from alcohol in needles, m.p. 223-25° (decomp.), yield 2.8 g. (95%). (Found : C, 68.9 ; H, 4.5. $C_{17}H_{14}O_5$ requires C, 68.5 ; H, 4.7%). The *acetyl* derivative was crystallised from alcohol in tiny needles, m.p. 156-57°. (Found : C, 66.8 ; H, 4.2. $C_{19}H_{16}O_6$ requires C, 67.1 ; H, 4.7%).

6-Methoxy-2-(2-hydroxy-4-methoxybenzyl)-coumaranone (VIII ; R_1 = OMe ; R_2 = H).—The reduction of 6-methoxy-2-(2-hydroxybenzylidene)-coumaranone was carried out by shaking its solution in alcohol (1 g. in about 250 c.c.) in an atmosphere of hydrogen in presence of palladium on charcoal, as described before. The resulting colorless solution was filtered and the filtrate diluted considerably with water when a crystalline material separated out. It was recrystallised from dilute methyl alcohol in colorless needles, m.p. 113-15°, yield 0.7-0.8 g. (65-70%). (Found : C, 64.0 ; H, 5.5. $C_{17}H_{16}O_5.H_2O$ requires C, 64.1 ; H, 5.7%).

7-Methoxy-2 : 3-(3' : 2' : 6'-methoxybenzofurano)-chromene (III : R_1 = OMe ; R_2 = H).—The preceding coumaranone (1 g.) was dissolved in hot dry benzene and P_2O_5 (*ca.* 2 g.) was added to the solution which was then refluxed on a water-bath for 2 hours, and then decanted off. On removal of benzene a crystalline solid was obtained which was recrystallised from methyl alcohol in colorless needles, m.p. 139-40°, yield 0.5 g. (55%). (Found : C, 72.4 ; H, 5.4. $C_{17}H_{14}O_4$ requires C, 72.4 ; H, 5.0%).

6-Methoxy-2-(2-hydroxy-4 : 6-dimethoxybenzylidene)-coumaranone (VII : R_1 = R_2 = OMe).—6-Methoxycoumaranone (1.64 g., 0.01 *M*) and 2-hydroxy-4 : 6-dimethoxybenzaldehyde (1.82 g., 0.01 *M*) were condensed as before and the orange-coloured crystalline solid so obtained was recrystallised from dilute acetic acid, m.p. 173-74°, yield 2.3 g. (70%). (Found : C, 65.9 ; H, 5.2. $C_{18}H_{16}O_6$ requires C, 65.9 ; H, 4.9%). The *acetyl* derivative was crystallised from alcohol in colorless needles, m.p. 135-37°. (Found : C, 64.4 ; H, 4.9. $C_{20}H_{20}O_7$ requires C, 64.5 ; H, 5.4%).

6-Methoxy-2-(2-hydroxy-4 : 6-dimethoxybenzyl)-coumaranone (VIII : R_1 = R_2 = OMe). —The reduction of the preceding coumaranone (1 g.), when carried out as described before, afforded a colorless crystalline solid which was recrystallised from aqueous methyl alcohol, m.p. 170-72°, yield 0.7 g. (70%). (Found : C, 64.9 ; H, 5.5. $C_{18}H_{18}O_6$ requires C, 64.5 ; H, 5.5%).

5 : 7-Dimethoxy-2 : 3-(3' : 2' : 6'-methoxybenzofurano)-chromene (III : R_1 = R_2 = OMe). —To the hot solution of the above coumaranone (1 g.) in dry benzene P_2O_5 (*ca.* 2 g.) was added and after refluxing for 2 hours, the solution was decanted off. On removal of benzene a solid was obtained which was crystallised from aqueous methyl alcohol in colorless needles, m.p. 160-62°, yield 0.6 g. (70%). (Found : C, 69.5 ; H, 5.1. $C_{18}H_{16}O_5$ requires C, 69.2 ; H, 5.1%).

6-Methoxy-2-(2-hydroxynaphthylidene)-coumaranone.—6-Methoxycoumaranone (3.3 g., 0.02 *M*) and 2-hydroxy-1-naphthaldehyde (3.44 g., 0.02 *M*) were condensed as before. The product, an orange-coloured solid, was crystallised from dilute acetic acid in orange needles, m.p. 176-78°, yield 5.5 g. (85-90%). (Found : C, 75.4 ; H, 4.4. $C_{20}H_{14}O_4$ requires C, 75.5 ; H, 4.4%). The *acetyl* derivative was crystallised from alcohol in colorless needles, m.p. 147-49°. (Found : C, 73.3 H, 4.6. $C_{22}H_{16}O_5$ requires C, 73.3 ; H, 4.4%).

6-Methoxy-2-(2-hydroxynaphthyl)-coumaranone.—The reduction of the preceding coumaranone (1 g.), when carried out as described before, gave a colorless crystalline solid which was recrystallised from aqueous methyl alcohol in colorless needles, m.p. 167-68° (decomp.), yield 0.8 g., (80%). (Found : C, 74.7 ; H, 5.2. $C_{20}H_{16}O_4$ requires C, 75.0 ; H, 5.0%).

2 : 3-(2′ : 3′ : 6′-Methoxybenzofurano)-1-benzo-(f)-chromene.—6-Methoxy-2-(hydroxynaphthyl)-coumaranone (1 g.) was cyclised as before. The product, a colorless crystalline solid, was recrystallised from aqueous methyl alcohol in colorless needles, m.p. 182-83°, yield 0.7 g. (70%). (Found : C, 79.2 ; H, 4.7. $C_{20}H_{14}O_3$ requires C, 79.5 ; H, 4.6%).

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Received September 19, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

HETEROCYCLIC COMPOUNDS. PART XXXII. NITRATION AND BROMINATION OF 1-METHYL- AND 3-METHYL-1 : 2 : 3 : 4-TETRAHYDRO-5-ACRIDONES

By R. D. Desai, B. M. Desai and N. N. Naik

7-Nitro-1-methyl-, 7 : 9-dinitro-1-methyl-, 7-nitro-3-methyl-, 9-nitro-3-methyl-, 7 : 9-dinitro-3-methyl-, 7-bromo-1-methyl-, 7 : 9-dibromo-1-methyl-, 7-bromo-3-methyl-, 9 bromo-3-methyl- and 7 : 9-dibromo-3-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridones have been prepared by direct nitration and bromination of 1-methyl- and 3-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridones. Their constitutions have been proved by their synthesis from suitably substituted nitro- and bromo-anthranilic acids and 1- and 3-methyl*cyclo*hexanones.

Bromination and nitration of 1 : 2 : 3 : 4-tetrahydro 5-acridones have been extensively studied. Thus, Desai and Buksh (*Proc. Ind. Acad. Sci.*, 1939, **10A**, 262), Huges and Lions (*J. Proc. Roy. Soc.*, 1933, **71**, 458), Huggill and Plant (*J. Chem. Soc.*, 1939, 784) have prepared 7-bromo-, while Huggill and Plant (*loc. cit.*) have also prepared 7 : 9-dibromo-1 : 2 : 3 : 4-tetrahydro-5-acridone. Perkin and Sedgwick (*J. Chem. Soc.*, 1924, **125**, 2437), Travin and Magidson (*J. Gen. Chem U.S.S.R.*, 1937, **7**, 842) and Huges and Lions (*loc. cit.*) have prepared 7-nitro-1 : 2 : 3 : 4-tetrahydro-5-acridone. The 8-nitro and 6-nitro derivatives were prepared by Perkin and Sedgwick (*loc. cit.*), while the 9-nitro derivative was prepared by Travin and Magidson (*loc. cit.*). As the nitration and bromination of 1 : 2 : 3 : 4-tetrahydro-5 acridones with a methyl substituent in the reduced benzene ring do not seem to have been studied, we have tried to prepare several nitro and bromo derivatives of 1-methyl- and 3-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridones.

1-Methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone on nitration gave 7-nitro-1-methyl and 7 : 9-dinitro-1-methyl derivatives. Similarly, 3-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone gave 7 nitro-3-methyl, 9-nitro-3-methyl and 7 : 9-dinitro-3-methyl derivatives. The constitutions of these compounds have been proved by their independent synthesis by condensing 5-nitro-, 3-nitro- and 3 : 5-dinitro-anthranilic acids with 1-methyl- and 3-methyl*cyclo*hexanones and comparing their melting and mixed melting points.

The bromination of 1-methyl- and 3-methyl-1 : 2 : 3 : 4-tetrahydro 5-acridones gave mainly 7-bromo derivatives, but in the case of 3-methylacridone another isomer, 9-bromo derivative, was obtained. 7 : 9-Dibromo derivatives were obtained on dibromination in both the cases. The constitutions were proved by preparing the authentic specimens by condensing 5-bromo-, 3-bromo- and 3 : 5 dibromo-anthranilic acids with 1-methyl- and 3-methyl-*cyclo*hexanones.

It is a general observation that an alkyl group exerts *ortho* and *para* directive influence, but as the methyl group is present in the reduced benzene ring, it is devoid of any influence and the nitration and bromination are mainly governed by the ring nitrogen atom.

EXPERIMENTAL

7-Nitro-1-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone.—1-Methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone (2.2 g.) was dissolved in H_2SO_4 (*d* 1.84, 15 c.c.). A mixture of HNO_3 (conc., 0.42 c.c.) and H_2SO_4 (conc., 5.0 c.c.), cooled to $-5°$, was added to the cooled solution of the acridone with constant shaking. After keeping the flask in ice-box for 14 hours, the mixture was poured on crushed ice. The precipitated solid was filtered, washed, dried and then crystallised from toluene in bright yellow leaflets, m.p. 310°. (Found : N, 10.76. $C_{14}H_{14}O_3N_2$ requires N, 10.85%).

Synthesis of 1-Methyl-7-nitro-1 : 2 : 3 : 4-tetrahydro-5-acridone.—5-Nitroanthranilic acid (3.6 g.) and 1 methyl*cyclo*hexanone (2.3 g.) were heated at 130-40° for 2 hours and then at 220-30° for further one hour. The solid was extracted with a little alcohol to remove the impurities. The product was crystallised from toluene in yellow leaflets m.p. 310°, undepressed by admixture with the mononitro derivative.

7 : 9-Dinitro-1-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone.—1-Methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone was dinitrated in the same manner by taking the acridone (2.2 g.) and the nitrating mixture (0.84 c.c. of HNO_3 + 5 c.c. of H_2SO_4). The product was crystallised from alcohol in yellow leaflets, m.p. 315°. (Found : N, 14.1. $C_{14}H_{13}O_5N_3$ requires N, 14.33%).

Synthesis of 7 : 9-Dinitro-1-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone.—3 : 5-Dinitroanthranilic acid (1.5 g.) and 1-methyl*cyclo*hexanone (2.3 g.) were heated at 130-40° for 2 hours and finally at 220-30° to complete the reaction. The substance was crystallised from alcohol in yellow leaflets, m.p. 315°. The m.p. showed no depression when mixed with the dinitro derivative of the acridone.

7-Nitro-3-methyl- and 9-Nitro-3-methyl-1:2:3:4-tetrahydro-5-acridones.—3-Methylacridone (2.2 g.) was nitrated by the nitrating mixture (1.5 c.c. of conc. HNO_3 + 5.0 c.c. of conc. H_2SO_4), and then kept in an ice-box for 12 hours. The solid, obtained by pouring the mixture into water, was filtered, washed and dried in a vacuum desiccator. It crystallised from alcohol in orange-yellow micro-crystals, m.p. 324°. This was proved to be the 7-nitro derivative by its mixed m.p. with the compound obtained from 5-nitroanthranilic acid and 3-methyl*cyclo*hexanone. (Found : N, 10.70. $C_{14}H_{14}O_3N_2$ requires N, 10.85%).

The yellowish mother-liquor on concentration and cooling deposited a solid in nodules, which after several crystallisations furnished pale yellow needles, m.p. 236°. This was proved to be the 9-nitro derivative by its mixed m.p. with the authentic specimen. (Found : N, 10.71. $C_{14}H_{14}O_3N_2$ requires N, 10.85%).

The 3-methylacridone was dinitrated by taking the acridone (2.6 g.) and the nitrating mixture (0.84 c.c. HNO_3 and 5.0 c.c. H_2SO_4) in the same manner as described above. The product was crystallised from alcohol in yellow plates, m.p. 271° which showed no depression when taken with the authentic specimen. (Found : N, 14.50. $C_{14}H_{13}O_5N_3$ requires N, 14.33%).

7-Bromo-1-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone.—1-Methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone (2.2 g.) was dissolved in glacial acetic acid (12 c.c.) and cooled to 5°,

and a trace of iodine added. A 20% solution of bromine in acetic acid (5 c.c.) was added in one lot. The mixture was stirred for one hour at 10° and left in the ice-box for 24 hours. The light yellow precipitate, obtained by pouring the mixture in water, was filtered, dried and crystallised from alcohol in pale yellow needles, m.p. 292°. (Found: Br, 27.4. $C_{14}H_{14}ONBr$ requires Br, 27.40%).

Synthesis of 7-Bromo-1-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone.—A mixture of 5-bromoanthranilic acid (2.16 g.) and 1-methyl*cyclo*hexanone (1.12 g.) was heated at 180° for 1 hour and then at 230-40° for 45 minutes. The solid was crystallised from alcohol in yellowish needles, m.p. 291-92°, and showed no depression when taken with the monobromo derivative of the acridone.

7 : 9-Dibromo-1-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone.—The acridone (2.13 g.) was dibrominated by using a 20% bromine solution in glacial acetic acid (9.6 c.c.) as above. The compound crystallised from alcohol in pale yellow leaflets, m.p. 215°. (Found: Br, 42.92. $C_{14}H_{13}ONBr_2$ requires Br, 43.12%).

Synthesis of 7 : 9-Dibromo-1-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone.—A mixture of 3 : 5-dibromoanthranilic acid (2.63 g.) and 1-methyl*cyclo*hexanone (1.12 g.) was heated as above and the compound was obtained as yellowish leaflets, m.p. 215°. The m.p. was undepressed when taken with the dibromo derivative of the acridone.

7-Bromo-3-methyl- and 9-Bromo-3-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone.—To a solution of 3-methylacridone (4.26 g.) in glacial acetic acid (15 c.c.) a trace of iodine was added, followed by a 20% bromine solution (5.0 c.c.), as in the case of 1-methyl analogue. On pouring the mixture into water, a yellowish substance settled down which was filtered, washed with water and dried. When crystallised from alcohol (90%), colorless needles were obtained, m.p. 321°. This compound was proved to be the 7-bromo derivative by its mixed m.p. with the authentic specimen. (Found: Br, 27.35. $C_{14}H_{14}ONBr$ requires Br, 27.40%).

The mother-liquor on evaporation gave an amorphous mass which on crystallisation from a mixture of ethyl and methyl alcohols (2 : 1) gave shining prismatic needles, m.p. 317°, depressed to 301° by the 7-bromo derivative. (Found: Br, 27.35. $C_{14}H_{14}ONBr$ requires Br, 27.40%).

The m.p.s of the bromo derivatives were undepressed when taken with the authentic specimens.

7 : 9-Dibromo 3-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone.—7-Bromo-3-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridone (2.9 g.) was brominated by the 20% bromine solution (5 c.c.) at 50°. The solid obtained on pouring the mixture into water was filtered, washed and dried. It crystallised from alcohol in orange-yellow plates, m.p. 151°. It showed no depression in m.p. when taken with the authentic specimen. (Found: Br, 43.30. $C_{14}H_{13}ONBr_2$ requires Br, 43.12%).

The authors are thankful to the Governing Body of the Ahmedabad Education Society for the facilities given to them.

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Received November 5, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

ACID HYDROLYSIS OF ACETAMIDE

By Sameer Bose

The kinetics of the acid-catalysed hydrolysis of acetamide has been studied in water and in mixtures of water and miscible organic solvents. The acids used are nitric and hydrochloric which have been found to behave similarly. Since the acid hydrolysis is somewhat slow, high concentrations of the acids have been used and the rate has been observed to go through a maximum as the concentration of the acid is increased. Replacement of a part of water by organic solvents has very little effect on the concentration of the acid responsible for the maximum velocity. Probable mechanism of hydrolysis has been discussed.

Taylor (*J. Chem. Soc*, 1930, 2741) observed that aqueous solution of acetamide, when hydrolysed by hydrochloric acid, attained a maximum velocity by an acid concentration of 3.6*N*. Similar results were reported by Benrath (*Z. anorg. Chem.*, 1926, **151**, 53) and Euler *et al.* (*Z. physikal. Chem.*, 1928, **131**, 107), although they did not investigate this phenomenon so fully as Taylor did. Krieble *et al.* (*J. Amer. Chem. Soc.*, 1938, **60**, 2976) observed that other amides behaved similarly and that sulphuric acid also produced a maximum velocity. The present work was undertaken to ascertain the effect of nitric acid and to investigate the cause of this peculiar phenomenon by replacing a part of water by organic solvents.

Experimental

Procedure.—The reaction was followed by estimating the ammonium salts produced during hydrolysis by Kolthoff's formaldehyde method (Kolthoff and Stenger, "Volumetric Analysis", Vol. II, 1947, p. 158) with a slight modification. An aliquot of the reaction mixture was first neutralised with 1*N*-NaOH, using phenol red as indicator. The final end-point was adjusted with 0.1*N*-NaOH. This neutral solution containing ammonium salts was treated with an excess of neutral formaldehyde solution and the acid liberated was titrated with 0.1*N*-NaOH. The method afforded excellent results when synthetic mixtures of ammonium acetate and sodium nitrate were analysed. The error did not exceed 1%. Carbonate-free alkali, prepared by Sörensen's method (*Biochem. Z.*, 1909, **21**, 168) was used throughout.

Hydrolysis by Nitric Acid.—Dilute solutions of nitric acid do not oxidise acetamide. This was confirmed by hydrolysing completely a 0.1*M* solution of the amide with 3*N*-nitric acid at 25°, when the theoretical amount of ammonium acetate was obtained. Four different concentrations of the amide (0.05*M*-0.2*M*) were hydrolysed with varying concentrations of the acid. Unimolecular constants were calculated. It was seldom that any point averaged varied more than 5% from the mean. In any experiment the velocity constant recorded represents an average of at least six time intervals (in hours). The results are recorded in Table I. The maximum rate was observed with 3*N*-HNO_3. That observed by Krieble *et al.*

(*loc. cit.*) with HCl was at 2.91*N*. This indicates that unlike H_2SO_4, which gives the maximum velocity at 5.0*N*, HCl and HNO_3 behave in a similar manner.

TABLE I

Acetamide hydrolysis by aqueous HNO_3 *soln.* (25°).

Conc. of HNO_3.	Unimol. $K \times 10^3$ (time in hours).			
	(0.05*M*).	(0.1*M*).	(0.15*M*).	(0.2*M*).
0.10 *N*	2.7	2.6	2.6	2.5
0.25	6.4	6.3	6.2	6.2
0.5	12.6	12.5	12.3	12.3
1.0	18.2	18.2	18.1	17.8
2.0	27.0	27.1	27.2	26.8
2.5	28.5	28.2	28.1	28.0
3.0	30.0	29.8	29.8	29.6
3.5	29.1	28.8	28.6	28.6
4.0	26.8	26.7	26.5	26.4
4.5	25.2	25.0	25.1	25.1

Figures in parentheses refer to amide concentrations.

Hydrolysis by HCl *in presence of Organic Solvents.*—Methyl alcohol, ethyl alcohol and acetone were used for hydrolysis with HCl. The water content in every case was 50% by volume. The results as recorded in Table II show that the maximum velocity occurs at the same concentration of HCl even on changing the solvent, except in the case of acetone which lowers the rate of hydrolysis considerably and gives a maximum velocity at 2*N*-HCl.

TABLE II

Acetamide hydrolysis by HCl (25°).

Conc. of HCl.	Unimol. $K \times 10^3$ (time in hours).			
	MeOH-H_2O. (50 : 50).	EtOH-H_2O. (50 : 50).	(Acetone-H_2O. (50 : 50).	H_2O. (100%)
0.25 *N*	6.9	7.0	5.2	6.6
0.5	12.5	12.6	8.2	13.0
1.0	20.1	20.0	14.0	19.6
2.0	33.4	33.5	19.8	30.0
2.5	34.5	35.2	18.7	34.2
3.0	36.8	37.0	16.3	35.9
3.5	35.3	35.0	14.0	34.0
4.0	33.3	34.0	...	32.6

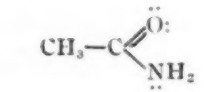
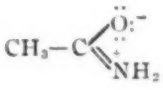
DISCUSSION

Taylor (*loc. cit.*) attributed the phenomenon of maximum velocity to the formation of a complex of acetamide with unionised molecules of HCl. The complex was considered to be stable and did not hydrolyse. He also stated that H_2SO_4 was not known to form such a complex and, hence, it did not produce a maximum velocity. Observations of Krieble *et al.* (*loc. cit.*) prove this statement regarding

H_2SO_4 to be erroneous. It is felt that even if acetamide combines with HCl, the compound formed will hydrolyse more or less completely in water because of its very weak basicity. Its calculated basic constant according to Pauling ("Nature of Chemical Bond", 1952, p. 208) is about 1×10^{-20}. p_H measurements made by the present worker also showed that even a large quantity of acetamide added to a 0.1*N* solution of HCl did not depress the hydrogen-ion concentration, when measurements were made immediately. Moreover, if a complex is at all formed then the maximum velocity should also depend on the amide concentration. This has been experimentally tested in the case of nitric acid and found untrue (Table I).

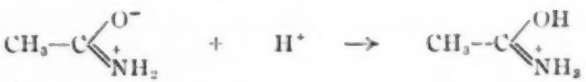
Krieble *et al.* (*loc. cit.*) in their explanation state that with a large increase in acid concentration, the activity of water falls which consequently lowers the velocity constant. The hydrolysis carried out in organic solvents like methyl and ethyl alcohol does not bear out this argument, because even on replacing half of the water by the solvent, the velocity constant practically remains unchanged. Hantzsch and Geidel (*Ber.*, 1931, **64B**, 667) claim that acetamide is a dimer existing in two forms: $CH_3.CO.NH_2$ (amino) and $CH_3.C(OH).NH$ imino). The two forms are in equilibrium. According to Krieble *et al.* (*loc. cit.*) the amino form combines with the excess of the acid, resulting in the diminution in the concentration of the imino form which, they claim, alone hydrolyses.

The recent observations on structure of amides (Pauling, *loc. cit.*, p. 133) show that it is improbable for them to resonate between the amino and the imino structures. The prarachor measurements of acetamide, made by Shukla and Bhatnagar (this *Journal*, 1955, **32**, 611), support the following structure ascribed by Pauling.

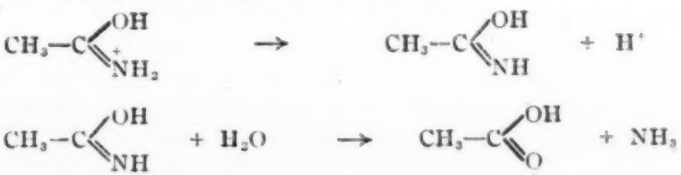
(A)  and (B) 

In amides the donor and acceptor groups are adjacent and so they resonate between the structures (A) and (B).

It is felt that the slight basic nature of acetamide is due to structure (A) and probably the structure (B) alone hydrolyses in the following manner:



The nitrogen atom under the influence of electromeric displacement becomes positively charged; hence, one of its hydrogen atoms tends to ionise.



The resonance between forms (A) and (B) will be completely inhibited by addition of a proton to the nitrogen atom and the amide will revert to structure (A). In presence of a large excess of acid such a situation arises with the consequence that the concentration of the unhydrolysable form (A) tends to increase. Taylor (*loc. cit.*) has observed that nitrous acid, which reacts with the basic NH_2 group in aliphatic amino compounds to give N_2, undergoes a reaction with acetamide only in presence of mineral acids and the rate of the reaction increases with increase in the concentration of the latter. This observation also supports the view that with increase in acid concentration (HCl or HNO_3), the concentration of the form (A), which is slightly basic, increases. This form being unhydrolysable, the rate of acid hydrolysis diminishes.

The thanks of the author are due to Dr. V. Gore for the facilities and to Dr. A. N. Kappanna for his interest in the work.

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Received October 16, 1957.

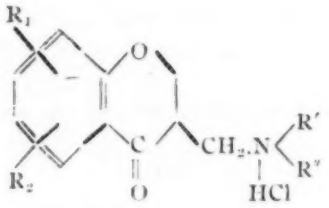
[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

POSSIBLE ANTIAMOEBIC AGENTS. PART IV. MANNICH BASES FROM SUBSTITUTED CHROMANONES

By A. B. Sen and S. L. Arora

Mannich bases from several substituted chromanones have been prepared with a view to testing their antiamoebic activity.

In continuation of the work carried out in this laboratory (Sen and Kulkarni, this *Journal*, 1957, **34**, 467) we have now extended this work to the preparation of the Mannich bases from methoxy-, alkyl-chloro-, iodochloro- and iodo-chromanones, with a view to studying the effect of these groups and their position in the nucleus on the antiamoebic activity. Several amoebacides (Entero-vioform, Diodoquin etc.) contain iodine in their molecule ; as such, iodine has been introduced in the nucleus of some of these compounds (I).



(I)

[R′ & R = various substituents in the basic side chain.
R_1 & R_2 = ,, ,, in the chromanone nucleus].

The present work reports the synthesis of β-(2-iodo-4-chloro-, 2-iodo- and 4-iodo-phenoxy)- propionic acids, their conversion into chromanones and the preparation of 6-chloro-7-methylchromanone.

The required β-phenoxypropionic acids were obtained by applying the method of Gresham *et al.* (*J. Amer. Chem. Soc.*, 1949, **71**, 661) from *o*-methoxy-, *p*-chloro-*m*-methyl-, *o*-iodo-*p*-chloro-, *o*-iodo- and *p*-iodo- phenols by condensing them with β-propiolactone in alkaline medium.

Only some of the β-phenoxypropionic acids could be cyclised by H_2SO_4 (conc., 98%) as described by Hurd and Hayao (*ibid.*, 1954, **76**, 5065). But in most of the cases, viz., β-(2-iodo-, 4-iodo- and 2-methoxyphenoxy)-propionic acids, cyclisation could not be effected with H_2SO_4 (conc.) satisfactorily, as treatment with it followed by dilution with crushed ice left a very small amount of a sticky black mass or in some cases no precipitate could be obtained. Cyclisation of these acids was effected with very good yields and purity by treating benzene solution of the β-phenoxypropionic acid with 5 parts of P_2O_5, as described by Robertson and Subramaniam (*J. Chem. Soc.*, 1936, 1832) and refluxing for 10 hours.

The Mannich base hydrochlorides of these chromanones were obtained by following the method of Harradence *et al.* (*J. Proc. Roy. Soc.*, N. S. Wales, 1939, **27**, 273) as modified by Sen and Kulkarni (*loc. cit.*); equimolar quantities of chromanones, paraformaldehyde and amine hydrochloride were suspended in dry benzene and acidified either by the addition of a few drops of HCl (conc.) or where this method did not succeed, HCl gas was passed. The reaction mixture was refluxed for 6 to 8 hours.

Experimental

The following phenols were used, viz., *o*-methoxy-, *p*-chloro-*m*-methyl-; 2-iodo-4-chlorophenol was obtained by the method of Verma and Yashoda (this *Journal*, 1939, **16**, 477); 2-iodophenol was obtained according to Gilman (Org. Syn., Vol. 1, 1932, p. 319) and 4-iodophenol was obtained by following the method as described by Vogel ("Practical Organic Chemistry", 1948, p. 651). β-Propiolactone was obtained from Eastman Kodak Ltd.

Substituted β-Phenoxypropionic Acids.—The β-phenoxypropionic acids were obtained from the corresponding phenols by condensing with β-propiolactone (Gresham, *loc. cit.*).

β-(3-Methyl-4-chlorophenoxy)-propionic acid has been reported by Hall *et al.* (*J. Chem. Soc.*, 1949, 2035), but we have prepared it by the condensation of the phenol with β-propiolactone.

The yields, m.p., neutralisation equivalents and the analytical data for these acids are recorded in Table I.

Table I

β-Phenoxypropionic acids.	M.P.	% Yield.	Neut. equiv. Found.	Neut. equiv. Calc.	% Carbon. Found	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
3-Methyl-4-chloro-	141°	50	214.1	214.5	55.70	55.90	5.00	5.13
2-Iodo-4-chloro-	136°	48	327.0	326.5	32.90	33.10	2.35	2.45
2-Iodo-	123°	45.5	291.7	292.0	37.20	37.00	3.20	3.08
4-Iodo-	160-61°	43	292.3	292.0	36.90	37.00	2.80	3.08

Substituted Chromanones

7-Methyl-6-chloro- and *8-iodo-6-chloro-chromanones* were obtained by cyclisation of the corresponding β-phenoxypropionic acids with H_2SO_4 (conc., 98%). In the first case the acid was treated with 10 parts whereas in the second case with 7.5 parts of H_2SO_4 (conc.) and the solution kept for 36 hours with occasional shaking at the room temperature. The chromanones were then isolated in the usual way, as described by Hurd and Hayao (*loc. cit.*).

8- & *6-Iodo-* and also *8-methoxy-chromanones* were obtained by the cyclisation of the corresponding β-phenoxypropionic acids with P_2O_5 in dry benzene according to the method described by Robertson and Subramaniam (*loc. cit.*).

8 Methoxychromanone has been reported by Wiley (*J. Amer. Chem. Soc.*, 1951, **73**, 4205).

The chromanones were characterised through their 2:4-dinitrophenylhydrazone.

The m.p., yields, m.p. of their 2:4-dinitrophenylhydrazones and the analytical data of these chromanones are recorded in Table III.

TABLE II

(Vide structure I)

Sl. No.	R_1 & R_2.	R′ & R″.	Acid medium.	M.P.	% Yield.	Mol. formula.	% Nitrogen.		Picrates.			
							Found.	Calc.	M.P.	Mol. formula.	% Nitrogen. Found.	% Nitrogen. Calc.
1.	8-Methoxy-	Morpholinyl-	(B)	174°	56.80	$C_{15}H_{20}ClNO_4$	4.28	4.46	155-56°	$C_{21}H_{22}N_4O_{11}$	11.10	11.07
2.	,,	Piperidyl-	,,	150°	25.00	$C_{16}H_{22}ClNO_3$	4.30	4.49	...			
3.	,,	Benzyl-	,,	209°	26.00	$C_{19}H_{20}ClNO_3$	4.10	4.20	...			
4.	7-Methyl-6-chloro-	Morpholinyl-	(A)	181°	53.00	$C_{15}H_{19}Cl_2NO_3$	4.04	4.22	152-53°	$C_{21}H_{21}ClN_4O_{10}$	10.45	10.68
5.	,,	Piperidyl-	,,	194°	40.00	$C_{16}H_{21}Cl_2NO_2$	4.30	4.24	154°	$C_{22}H_{23}ClN_4O_9$	10.50	10.71
6.	,,	Dimethyl-	,,	180°	29.00	$C_{13}H_{17}Cl_2NO_2$	4.41	4.81	...			
7.	6-Iodo-	Morpholinyl-	,,	189°	60.00	$C_{14}H_{17}ClINO_3$	3.21	3.42	162-63°	$C_{20}H_{19}IN_4O_{10}$	9.15	9.30
8.	,,	Piperidyl-	,,	201°	57.20	$C_{15}H_{19}ClINO_2$	3.32	3.43	...			
9.	,,	Dimethyl-	(B)	194°	33.00	$C_{12}H_{15}ClINO_2$	3.90	3.81	...			
10.	,,	Benzyl-	,,	201°	65.00	$C_{17}H_{17}ClINO_2$	3.09	3.26	...			
11.	8-Iodo-	Morpholinyl-	,,	191°	35.00	$C_{14}H_{17}ClINO_3$	3.36	3.42	139-40°	$C_{20}H_{19}IN_4O_{10}$	9.00	9.30
12.	8-Iodo-6-chloro-	Piperidyl-	,,	180°	30.00	$C_{15}H_{18}Cl_2INO_2$	3.20	3.17	...			
13.	,,	Morpholinyl	,,	Decomposes	30.00	$C_{14}H_{16}Cl_2INO_3$	3.15	3.15	...			
14.	,,	Dimethyl	,,	,,	10.00	$C_{12}H_{14}Cl_2INO_2$	3.50	3.48	...			

TABLE III

Substituted chromanones.	M.P.	% Yield.	% Carbon.		% Hydrogen.		2:4-Dinitrophenyl-hydrazone.		
			Found.	Calc..	Found.	Calc.	M.P.	% Nitrogen Found.	Calc.
7-Methyl-6-chloro-	55°	37.0	60.90	61.10	4.60	4.58	229-30°	14.70	14.90
8-Iodo-6-chloro-	110-11°	44.5	35.15	35.00	2.00	1.94	255-56°	11.30	11.46
6-Iodo-	84-85°	95.7	39.60	39.41	2.45	2.55	285-86°	12.20	12.31
8-Iodo-	109-10°	65.8	39.45	39.41	2.60	2.55	249-50°	12.15	12.34

Mannich Base Hydrochlorides from Substituted Chromanones (I)

These were obtained according to the method of Sen and Kulkarni (*loc. cit.*) as described below.

A mixture of the chromanone (0.01 *M*) and paraformaldehyde (0.01 *M*) in dry benzene (25 c.c.) was taken in a flask and refluxed for about 30 minutes. To this was added the amine hydrochloride (0.01 *M*) and refluxed again for about 10 minutes. It was then acidified either with 5 to 10 drops of HCl (conc., A.R) (A) or by passing dry HCl gas (B) and refluxing the reaction mixture for 6 to 8 hours, during which the Mannich base hydrochloride separated as fine crystalline mass in most of the cases. After the completion of the reaction, the reaction mixture was cooled and the crystalline mass filtered at the pump, washed with dry benzene, then with ether and finally recrystallised from absolute ethyl alcohol.

The Mannich bases (I) were characterised by preparing their picrates. The melting points, analysis of the Mannich base hydrochlorides and their picrates are recorded in Table II.

One of the authors (S.L.A.) expresses his grateful thanks to the U. P. Scientific Research Committee for the grant of a research assistantship and to the Professor of Chemistry for departmental facilities.

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Received August 28, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

VAPOUR PHASE CHLORINATION OF ETHANOL UNDER SILENT ELECTRIC DISCHARGE.* PART I. QUALITATIVE STUDIES

By O. P. Malhotra

Chlorination of ethanol has been carried out in vapour phase under silent electrical excitation. The products obtained have been found to contain ethyl acetate, di- and trichloroacetaldehydes, trichloroacetaldehyde alcoholate, paraldehyde, mono-, di- and trichloroacetaldehyde acetals, 1 : 2-di- and 1 : 2 : 2-trichlorodiethyl ethers, hexachlorethane, HCl and some organic acids besides unchanged ethanol.

A large amount of work has been reported in the literature on the chlorination of ethanol in liquid phase, a process exploited commercially for the manufacture of chloral and allied compounds. The present author has studied this reaction in the vapour phase under the silent electrical excitation. This communication deals with a detailed qualitative study of the products formed.

Experimental

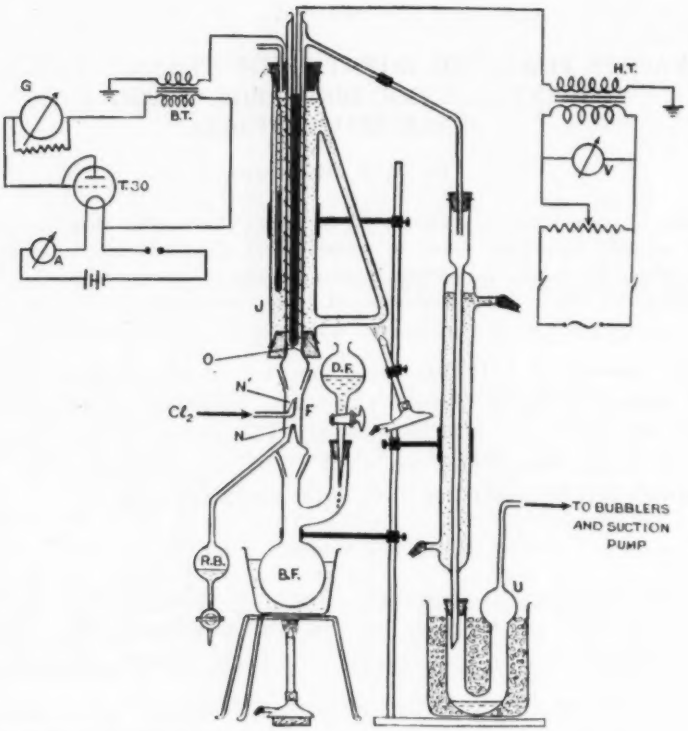
The glass apparatus and electrical circuit are shown in Fig. 1 which is self explanatory. A few points may, however, be mentioned. The discharge tube consists of a Siemens' type all-glass ozonizer (O) with the following dimensions :

External diameter of the outer tube	=	12 mm.
Internal	,,	,,	,,	,,	,,	=	9	
External	,,	,,	,,	inner	,,	=	6	
Internal	,,	,,	,,	,,	,,	=	4	
Average length of the ozonizer						=	350	(approx.)

The two feeding nozzles, N and N′ (for alcohol vapour and chlorine respectively), were drawn into fine jets so as to avoid back diffusion, and N was fitted internally into the feeder in such a way that any liquid trickling down the ozonizer was collected in a separate receiving bulb (R.B.) and could not go back to the boiling flask (B.F.). Size of the feeder was kept minimum possible and asbestos wound round it to avoid condensation of alcohol vapour. The uncondensed gases emerging from U-tube (U), cooled in powdered ice, were passed through a water-filled Dreschel bottle (not shown in the fig.) to absorb water-soluble gases and then bubbled through a strong solution of sodium hydroxide (to remove unchanged chlorine) before being sucked up by a water filter pump which helped to maintain a uniform flow of gases through the system ; a safety bottle was interposed before each bubbler.

* A brief report of preliminary investigations has already been published by Malhotra and Trived. (*Curr. Sci.*, 1955, **35**, 337).

FIG. 1



H.T. High tension transformer.
B.T. Bell transformer.
G. Galvanometer.
D.F. Dropping funnel.
O. Ozoniser.
J. Water jacket.
R.B. Receiving bulb
B.F. Boiling flask.
U. U-tube.
F. Feeder.
N, N'. Feeding nozzles.

Alcohol was fed from the dropping funnel (D.F.) at the rate of 4 c.c./hour and chlorine, preheated to 80° (approx.), passed at 6 c.c./sec. (as measured by a flow-meter, not shown in the fig.). The ozonizer was maintained at 80-90° and a steady discharge was passed through it at 2.6 kV (500 cycles/sec. A.C.), a potential slightly higher than the threshold potential required for the dielectric breakdown of the gases.

Products collected.—A yellowish brown viscous liquid with a sharp pungent smell (of HCl) was obtained by mixing the products collected in the U-tube (U) and the bulb (R.B.). It was strongly acidic and fumed in moist air. The entire product, after neutralisation with excess of pure calcium carbonate, was fractionated repeatedly and the fractions identified by usual methods. Starting from 100 c.c. of the products, the amounts of different fractions and the compounds identified in each have been recorded in Table I.

TABLE I

Analysis of the products.

Volume of discharge products taken = 100 c.c.

	Temp. range.	Volume.	Compounds identified.
1.	Below 78° (mainly 76-78°)	8 c.c.	Ethyl acetate + ethanol
2.	78-80°	35	Ethanol
3.	80-85°	4	Ethanol + dichloroacetaldehyde
4.	89-94°	4	Dichloroacetaldehyde
5.	96-100°	6	Trichloroacetaldehyde (chloral
6.	114-116°	1	Trichloroacetaldehyde alcoholate
7.	120-150°	0.5	Paraldehyde*
8.	156-164°	10	Monochloroacetaldehyde acetal + 1 : 2-dichlorodiethyl ether* + 1 : 2 : 2-trichlorodiethyl ether*
9.	175-185°	25	Dichloroacetaldehyde acetal
10.	Residue	1	Trichloroacetaldehyde acetal

* Confirmatory tests for these compounds could not be performed for want of sufficient material.

Free Acidity.—Several runs of the discharge products (8 c.c. each), collected at different potentials, were diluted (volume made up to 100 c.c.) and separately analysed volumetrically for H^+ and Cl^- ions to ascertain if the acidic nature of the products was due entirely to HCl or some other acids were present beside it. The normalities of these two ions in the different runs have been recorded in Table II.

TABLE II

Estimation of H^+ *and* Cl^- *ions.*

Sr No.	1	2	3	4	5	6	7	8
H^+ (normality)	0.5601	0.4849	0.4301	0.5261	0.4446	0.4823	0.5924	0.3965
Cl^- (,,)	0.5520	0.4630	0.4244	0.5058	0.4308	0.4741	0.5733	0.3810
Diff. (,,)	0.0081	0.0291	0.0057	0.0203	0.0138	0.0082	0.0192	0.0155

The value of H^+ ion normality being invariably higher than that of Cl^- ions, the presence of some other acids, possibly organic carboxylic acids, was indicated, and confirmed by spot tests, viz., the two ferric chloride tests (Fiegel, Anger and Frehden, *Mikrochem.*, 1934, **15**, 18; cf. Davidson, *J. Chem. Ed.*, 1940, **17**, 81; Fiegel, "Spot Tests", 3rd ed., 1947, p. 399) and the lanthanam nitrate test (Kruger and Tschirch, *Ber.*, 1929, **62**, 2770; 1930, **63**, 826; *Mikrochem.*, 1930, **8**, 218). The indigo test with *o*-nitrobenzaldehyde (Fiegel, Sanchez and Zappert, *Mikrochem.*, 1935, **17**, 165), however, was negative, thus indicating the absence of acetic acid. As no specific tests for chlorine-substituted acetic acids were available, no distinction could be made between them.

Presence of Hexachloroethane.—Distillation of the discharge products without neutralisation left a dark residue which on standing deposited white camphoraceous smelling crystals. Such crystals, obtained from about 100 c.c. of the products,

were washed with water and recrystallised from aqueous alcohol. The solid melted at 186° (in a sealed tube) and did not lower the m.p. of an authentic sample of hexachloroethane (m.p. 186-87° in a sealed tube) (Huntress, "Organic Chlorine Compounds", John Wiley, 1948, p. 439).

Analysis of Water Washings.—Water washings of the exit gases, after being neutralised with calcium carbonate, were distilled and the fraction boiling below 98° was treated with a large excess of anhydrous copper sulphate and extracted with ether. The solvent was evaporated off and the residue (about 0.5 c.c.) was identified as chloral. The rest of the water washings distilled at 98°-100° and consisted mostly of water.

Further work and the mechanism of this reaction will appear in a later communication.

The author is grateful to Prof. S. S. Joshi, D.Sc., F.R.I.C., F.N.I., Head of the Chemistry Department, the Banaras Hindu University, for suggesting the problem and guidance. Sincere thanks of the author are also due to Dr. R. H. Sahasrabuddhe, D.Sc., for criticism.

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Received September 21, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

STUDIES ON THE NATURE OF THE RACEMIC MODIFICATIONS OF OPTICALLY ACTIVE COMPOUNDS IN SOLID STATE. PART XVI. *p*-SULPHONAMIDO-, *o*-, *m*-, *p*-METHOXY , *o*-, *m*-, *p*-ETHOXY-PHENYLIMINOCAMPHORS (*d*- & *dl*-) AND *p*-SULPHONAMIDO *o*- AND *p*-METHOXY-PHENYLAMINOCAMPHORS (*d*- & *dl*-)

By Bawa Kartar Singh and Bhupendra Sahai Saxena

The nature of the racemic forms of *p*-sulphonamido-, *o*-, *m*-, *p*-methoxy-, *o* , *m*-, *p*-ethoxy-phenyliminocamphors and *p*-sulphonamido-, *o*- and *p*-methoxy-phenylaminocamphors has been studied by the application of the melting point—composition method of Roozeboom. The racemic modifications of *o*- and *m*-ethoxyphenyliminocamphors have been found to be solid solutions giving single continuous curves with a central maximum, whereas the remaining forms are true *dl*-compounds of varying stability.

The nature of the racemic modifications of *p*-sulphonamido-, *o*-, *m*-, *p*-methoxy-, and *o*-, *m*-, *p*-ethoxy-phenyliminocamphors and *p*-sulphonamido-, *o*- and *p*-methoxy-phenylaminocamphors has been discussed in the present communication by studying the freezing point—composition diagrams based on the method adopted by Roozeboom (*Ber.*, 1899, **32**, 537 ; *Z. physikal. Chem.*, 1899, **28**, 494). It is observed that if the melting point—composition diagram is composed of (*i*) three curves, the racemic modification is a true *dl-compound*, (*ii*) two curves, it is a *conglomerate* or *mechanical mixture* of equimolecular quantities of the *dextro* and *laevo* forms and (*iii*) one curve, a *solid solution* or *mixed crystals* of the active and opposite isomers in equimolecular proportions.

Whereas we have not met with any example of the racemic form existing as mechanical mixture, *o*- and *m*-ethoxyphenylimino-*dl*-camphors are found to be solid solutions, and the racemic modifications of the remaining compounds are true *dl*-compounds.

Since each diagram is symmetrical, only the *dextro* forms together with the *racemic* modifications have been taken for the study : the half portion of each diagram is represented by *d*— *dl* and *dl*—*d* curves ; the remaining part, *di*—*l* and *l*—*dl*, represented by dotted curves, is drawn as a mirror image of the first half.

Experimental

All the racemic forms, with the exception of *p*-sulphonamidophenylimino-*dl*-camphor prepared by Singh and Manhas (*Proc. Ind. Acad. Sci.*, 1949, **30A**, 87), are new substances.

Amongst the *dextro* derivatives, the following are new compounds : *p*-sulphonamidophenylamino-*d*-camphor and *m*-methoxy-, *o*- and *m*-ethoxy-phenylimino-*d*-camphors. The physical properties and analyses of all the compounds are recorded in Table I.

TABLE I

No.	The compounds and molecular formulae.		M.P.	Co'our.	Cryst. form.	% Nitrogen Found.	% Nitrogen Calc.	Remarks
1.	*p*-Sulphonamidophenylimino-camphors*, $C_{16}H_{20}N_2SO_3$	*d*-	228°	Pale yellow	Thin rectangular plates	9.08	8.75	A. *Solubility* :-All the aryl-*imino* compounds are highly soluble in chloroform, acetone, ethyl acetate, benzene and pyridine; less so in methyl and ethyl alcohols and insoluble in water. While their solutions in benzene and pyridine are deep orange, in other solvents they are lemon-yellow. The aryl-*amino* compounds are fairly soluble in all organic solvents except *p*-sulphonamido-phenylamino-camphors in benzene in which they are almost insoluble.
		dl-	227.5°	Yellow	Thin hexagonal plates	8.93		
2.	*p*-Sulphonamidophenylamino-camphors, $C_{16}H_{22}N_2SO_3$	*d*-	181.5°	Colorless	Long prismatic needles	9.10	8.70	
		dl-	185.5°	Colorless	Rectangular plates	8.95		
3.	*o*-Methoxyphenylimino-camphors, $C_{17}H_{21}NO_2$	*d*-**	120°	Yellow	Leaflets	5.54	5.17	
4.	*m*-Methoxyphenylimino-camphors, $C_{17}H_{21}NO_2$	*dl*-	118°	Yellow	Leaflets	5.33		
		d-	78.5°	Yellow	Silky needles	5.33		
		dl-	97.5°	Golden yellow	Cubes	5.41		
5.	*p*-Methoxyphenylimino-camphors, $C_{17}H_{21}NO_2$	*d*-α	114.5°	Yellow	Leaflets	5.29		
		d-β‡	120°	Golden yellow	Prismatic needles	...		
		dl-	130°	Golden yellow	Hexagonal plates	5.44		
6.	*o*-Methoxyphenylamino-camphors, $C_{17}H_{23}NO_2$	*d*-§	148°	Colorless	Long shining needles	...	5.13	B. *Liquid compounds* :-The *m*-methoxy-phenylaminocamphors (*d* and *dl*) and also the *o*-, *m*- and *p*-ethoxyphenyl-aminocamphors (*d* and *dl*) were prepared by the usual methods, but being liquids, they could not be included in the present study.
		dl-	134°	Colorless	Prismatic needles	5.37		
7.	*p*-Methoxyphenylamino-camphors, $C_{17}H_{23}NO_2$	*d*-‡	101°	Colorless	Thin plates	5.38		
		dl-	108.5°	Colorless	Plates	5.40		
8.	*o*-Ethoxyphenylimino-camphors, $C_{18}H_{23}NO_2$	*d*-	53°	Bright yellow	Leaflets	5.16	4.91	
		dl-	59°	Bright yellow	Leaflets	5.19		
9.	*m*-Ethoxyphenylimino-camphors, $C_{18}H_{23}NO_2$	*d*-	82.5°	Yellow	Fine needles	5.14		
		dl-	120.5°	Deep yellow	Prismatic needles	5.18		
10.	*p*-Ethoxyphenylimino-camphors, $C_{18}H_{23}NO_2$	*d*-‡	112°	Bright yellow	Silky leaflets	...		
		dl-	111°	Golden yellow	Prismatic needles	5.18		

C. *Melting points* :-The melting point of *p*-sulphonamidophenylimino-*dl*-camphor has been reported by Singh and Manhas* to be 240°, whereas we find it to be 227.5°. Similarly the melting point of *o*-methoxyphenylimino-*d*-camphor, reported 125-26° by Singh and Mazumder**, was found to be 120°.

* Singh and Manhas (*loc. cit.*).

** Singh and Mazumder (*loc.cit.*).

‡ Forster and Thornley (*loc cit*).

§ Singh, B.K. *et al.*, *J. Chem. Soc.*, 1920, **117**, 980.

The different *imino* compounds were prepared by condensing the camphorquinones (*d*- and *dl*-) with the following bases: *p*-aminobenzenesulphonamide, *o*-, *m*-, *p*-anisidines and *o*-, *m*-, *p*-phenetidines, by one of the two methods described below.

(*a*). *Condensation of the Free Base with Camphorquinone.*—The free base, with an equimolecular quantity of camphorquinone (*d*- or *dl*-) was heated in the presence of an excess of anhydrous sodium sulphate in an oil-bath at 120-40° for 12 to 16 hours. The product was extracted with water and the residue crystallised from rectified spirit. This method was unsuccessful in the case of *o*- and *m*-methoxyphenylimino-*d*-camphors and *o*-, *m*- and *p*-ethoxy-phenyliminocamphors (*d*- and *dl*-).

(*b*). *Condensation of the Hydrochloride of the Base with Camphorquinone.*—This method, much more effective than the first, consisted in heating equimolecular quantites of camphorquinone (*d*- or *dl*) and the hydrochloride of the base with an excess of fused sodium acetate on a water-bath for 2 to 4 hours. The product was washed with water and the yellow-coloured residue crystallised from alcohol. This method was applicable for all the compounds except in the case of *p*-sulphonamidophenyliminocamphors (*d*- and *dl*-) where the hydrochloride could not be prepared due to insolubility of the base in ether and other organic solvents.

A marked difference in the reactivity of *d*- and *dl*-camphorquinones was observed. The *dl*-camphorquinone was found to be more reactive than the *d*-form by the comparatively short time required for condensation. Whereas *dl*-camphorquinone condensed easily with *o* and *m*-anisidines by the free base method, *d*-camphorquinone did not; for the preparation of *o*- and *m*-methoxyphenylimino-*d*-camphors therefore, the hydrochloride method was applied.

The aryl-*amino* derivatives were prepared by reduction of the corresponding *imino* compounds by the following two methods:

The acid reduction gave generally poor yields as in the case of *p*-methoxyphenylamino-*d*-camphor, prepared by Forster and Thornley (*J. Chem. Soc.*, 1909, **95**, 952). The alkaline reduction method was therefore applied in all the cases, except in the case of *p*-sulphonamidophenylaminocamphors (*d*- and *dl*-) where the *amino* compounds were insoluble in ether.

p-*Sulphonamidophenylaminocamphors* (*d*- and *dl*-) were prepared by the acid reduction method of Forster and Thornley (*loc. cit.*).

The *o*- and *p*-methoxyphenylaminocamphors (*d*- and *dl*-) were prepared by the alkaline reduction method after Singh and Mazumder (*J. Chem. Soc.*, 1919, **115**, 566).

p-Methoxyphenylimino-*d*-camphor exists in dimorphic forms (Table I). Both the forms were prepared in the same way except for some difference in crystallisation of the crude product. Recrystallisation from absolute or 90% aqueous alcohol gave the β-form (m.p. 120°), while more dilute alcohol solutions (about 50%) deposited the α-form (m.p. 114.5°).

Mutual Transformation of α- and β-Forms

(*i*). α-Form was converted into β-form by recrystallisation from absolute or 90% alcohol.

(*ii*). α-Form changed into β-form by heating it at its melting point with a trace of β-form.

(*iii*). α-Form on being kept in molten state for sometime gave β-form.

(*iv*). β-Form on recrystallisation form dilute alcohol (50%) gave α-form.

DISCUSSION

Nature of the Racemic Forms

p-*Sulphonamidophenylimino- and -aminocamphors*.—The melting point—composition diagrams of the aryl-*iminocamphors* (Fig. 1-a) and the corresponding *amino*-

FIG. 1

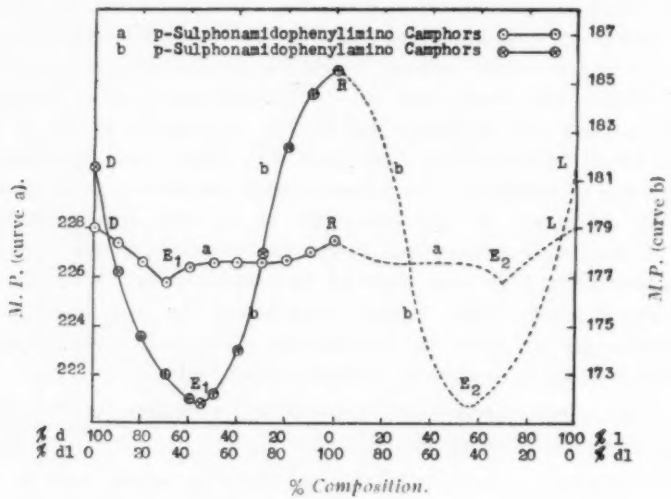
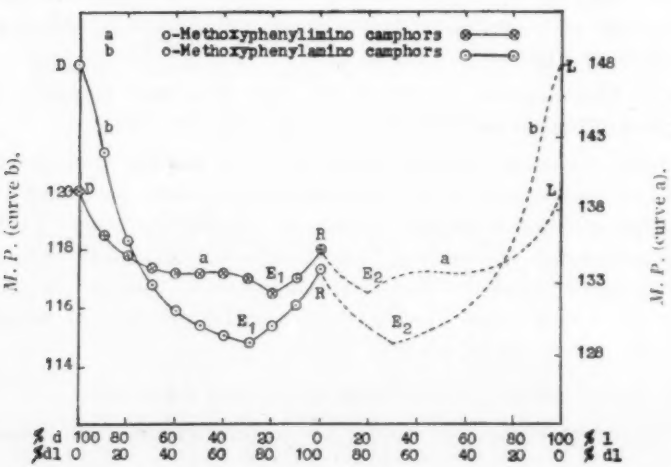

a p-Sulphonamidophenylimino Camphors
b p-Sulphonamidophenylamino Camphors
M. P. (curve a).
M.P. (curve b)
% d 100 80 60 40 20 0 20 40 60 80 100 % l
% dl 0 20 40 60 80 100 80 60 40 20 0 % dl
% Composition.

FIG. 2

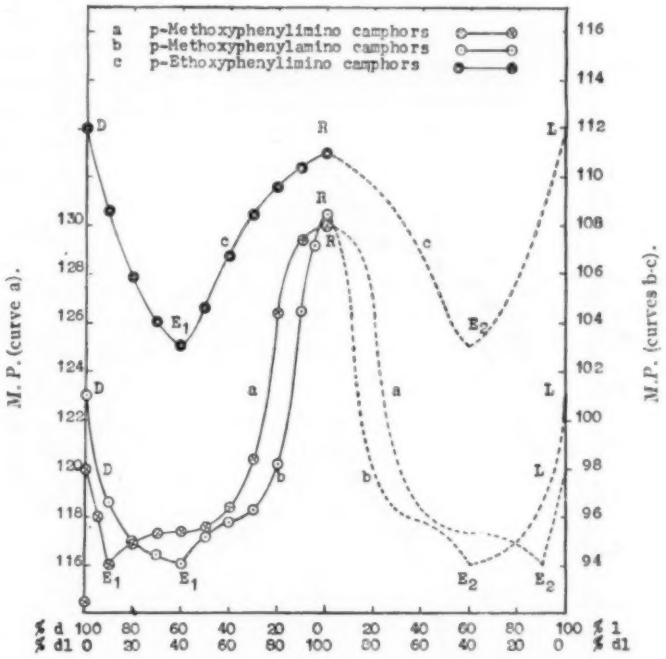

a o-Methoxyphenylimino camphors
b o-Methoxyphenylamino camphors
M. P. (curve b).
M. P. (curve a).
% d 100 80 60 40 20 0 20 40 60 80 100 % l
% dl 0 20 40 60 80 100 80 60 40 20 0 % dl
% Composition.

camphors (Fig. 1-b) consist of three curves, DE_1, E_1RE_2 and E_2L in each case with a central maximum R and two sharp and well-defined eutectic points, E_1 and E_2; this shows that the racemic forms of both the compounds are true *dl*-compounds.

In the case of aryl-*amino* compound (Fig. 1-b), the *dl—d* curve is steep, showing that the *dl*-compound is stable and does not dissociate appreciably at its melting point, whereas the *dl—d* curve of the aryl-*imino* derivative is practically flat, specially in the region 50*d* : 50*dl* to 30*d* : 70*dl*, indicating a tendency to form solid solutions between the *dextro* and *racemic* isomers in this region.

The aryl-*amino* racemate is much more stable than the corresponding *imino* derivative as the area under the central part of the diagram is much greater in the former than in the latter.

FIG. 3

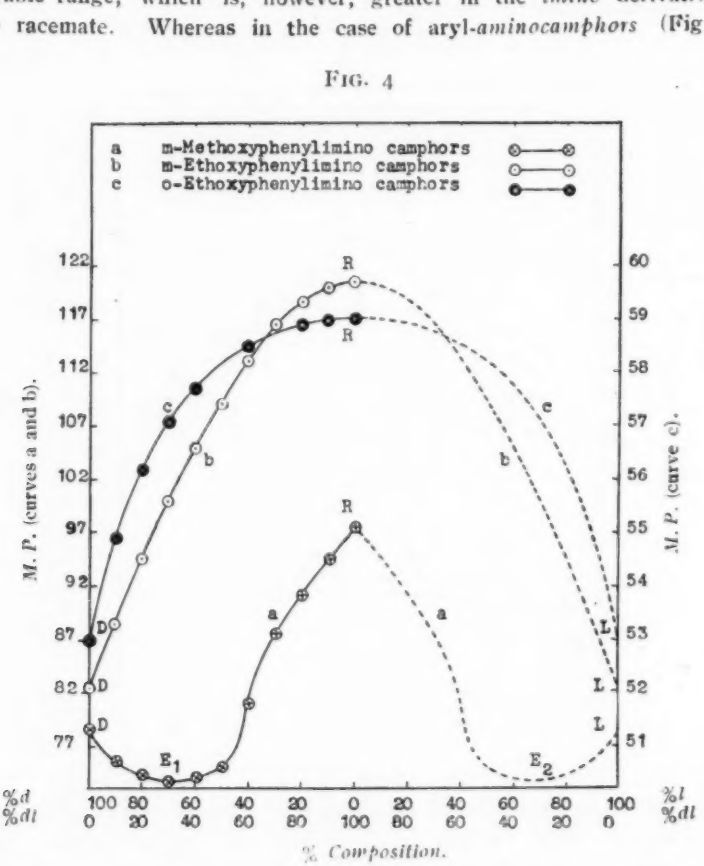


o-*Methoxyphenylimino- and -aminocamphors.*—The diagrams of each of these compounds (Fig. 2-a and 2-b) consist of three curves, DE_1, E_1RE_2 and E_2L with a central maximum R, indicating these racemic forms to be true *dl*-compounds. The central portions of these diagrams are almost similar in shape, occupying relatively small areas and the *dl—d* curves are steep; these racemic forms are therefore stable at the melting point, but the range of stability is not large, being lower in *imino* than in the corresponding *amino* derivative.

In the case of the *imino* compound (Fig. 2-a), the *d—dl* curve is horizontal in the range 60*d* : 40*dl* to 40*d* : 60*dl* ; this points to the fact that the racemic compound and the optically active form give solid solutions in this region. Both the diagrams, however, have sharp and well-defined eutectic points, E_1 and E_2.

p-*Methoxyphenylimino- and -aminocamphors.*—The diagrams of these compounds (Fig. 3-a and 3-b) consist of three curves with a central maximum point as in the case of *ortho* and *meta* compounds ; the racemic forms are therefore true *dl*-compounds. In both the diagrams, the *dl—d* curves are steep and the areas covered by the central portions large, being greater in *imino* than in the corresponding *amino* derivative. This shows that the racemic compounds are stable over a considerable range, which is, however, greater in the *imino* derivative than in the *amino* racemate. Whereas in the case of aryl-*aminocamphors* (Fig. 3-b) the

FIG. 4



central top portion of the curve is quite pointed, showing practically no dissociation of the racemic form ; in the case of the corresponding *iminocamphors* (Fig. 3-a), this part is somewhat rounded, indicating that the racemic compound dissociates, to some extent, to the optically active and opposite forms near its melting point.

The *p*-methoxyphenylimino-*d*-camphor exists in dimorphic forms (α and β). These forms are mutually interconvertible as described in the experimental part. The racemic modification with each of these α- and β-forms gives identical and superposable curves (Fig. 3-a). This shows that the *transition temperature* is *below* the melting points of the mixtures (Singh and Seth, this *Journal*, 1956, **33**, 491 ; Singh and Verma, *Proc. Ind. Acad. Sci.*, 1956, **43A**, 21).

m-*Methoxyphenyliminocamphors*.—This diagram (Fig. 4-a) is made up of three curves, DE_1, E_1RE_2 and E_2L with a central maximum R, showing that the racemic form is a true *dl*-compound. The steep slope of the *dl*—*d* curve and the large area occupied by the central part of the diagram indicate that the *dl*-compound is stable over a wide range. No sharp and well-defined eutectic points can be observed at E_1 and E_2 ; this shows that the racemic compound has a tendency to form solid solutions with the active form in this region.

o-, m- & p-*Ethoxyphenyliminocamphors*.—Whereas the melting point—composition diagrams of *ortho* (Fig. 4-c) and *meta* (Fig. 4-b) isomers consist of single continuous curves with a maximum, indicating these racemic modifications to be solid solutions of equimolecular quantities of the *dextro* and *laevo* forms, that of the *para* isomer (Fig. 3-c) consists of three curves, DE_1, E_1RE_2 and E_2L with a central maximum R and two sharp and well-defined eutectic points, E_1 and E_2 ; the racemic form in this case is therefore a true *dl*-compound. As the central part of the diagram occupies a fairly large area, the range of stability of the racemic compound is considerable.

The authors wish to make a grateful acknowledgement to the Banaras Hindu University for the provision of research facilities and to the Scientific Research Committee, Uttar Pradesh, for the grant of a research assistantship to one of them (B.S. Saxena).

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Received July 5, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

SEARCH FOR NEW ANTIBACTERIAL COMPOUNDS. PART II. EVALUATION OF THE ANTIBACTERIAL ACTIVITY OF NEW PHENOLS

By S. S. Tiwari, A. Mukerji and Brajendra Nath Tripathi

The bacteriostatic activity of 2-alkyl-3-methyl-6-*tert.*-butylphenols and 2-alkyl-4-*tert.*-butyl-6-chlorophenols against various bacteria has been determined. Three phenols found to be comparatively active, have been evaluated for their Rideal-Walker coefficients.

In the cases of xylenols, the germicidal activity against *Staphylococcus aureus* increases more rapidly with branched chain compounds, and in the cases of dihydroxy derivatives, branched chain compounds have been reported to possess unusually high activity (Baichwal, Jhavery and Khorana, *J. Sci. Ind. Res.*, 1951, **10**, 498). Klarmann, Sternov and Gates (*J. Lab. Clin. Med.*, 1933, **19**, 835; 1934, **20**, 40) showed that *para*-alkyl derivatives of *ortho*-chlorophenols were efficient germicides. Hence, various 2-alkyl-3 methyl-6-*tert* -butylphenols (this *Journal*, 1954, **31**, 79) and 2-alkyl-4-*tert.*-butyl-6-chlorophenols (*ibid.*, 1956, **33**, 211) have been tested for their bacteriostatic action against *Streptococcus haemolyticus*, *Staphylococcus aureus*, *Pseudomonas pyocyaneous* and *Salmonella typhi* or *Bacillus subtilis*, following the procedure of Mukerji (*Ind. Med. Gazz.*, 1954, **89**, 415) at the dilutions of 1/100, 1/500, 1/1000, 1/2000, 1/5000 and 1/10, 000 in 3% agar medium.

Bean and Berry (*J. Pharmacol.*, 1951, **3**, 639, 55) have found that the maximum activity of a halogenated phenol, solubilised by aqueous soap solution, is exhibited at the critical concentration of the soap. The activity of the halogenated phenol is related to its concentration in the micelles of soap and is independent of the overall concentration. In the experiments reported here, the colloidal agar served more or less the same purpose as the soap micelles. It is postulated that under these circumstances the bacteria are affected by the way of the Donnan membrane. The semipermeable bacterial wall with its own surface charge acts as a membrane and exchange occurs between phenol presented to the bacteria by the agar or the soap micelle and the inner substances within the bacteria.

2-Butyl-3-methyl-6-*tert.*-butylphenol, 2-butyl-4-*tert.*-butyl-6-chlorophenol and 2-octyl-4-*tert.*-butyl-6-chlorophenol have been found to be active against *S. haemolyticus* and *S. aureus* even in dilutions between 1/5000 and 1/10,000. Hence, these were evaluated for their Rideal-Walker coefficients.

TABLE I

Bacteriostatic activitiy of phenols.

No.	Phenols.		*Strep. haem.*	*Staph. aur.*	*Pseudo. pyoc.*	*Sal. typhi.*	*Bac. subtil.*
1.	2-Ethyl-P	No growth	1/1000	1/1000	1/500	1/1000	...
		Growth	1/2000	1/2000	1/1000	1/2000	1/100(T)
2.	2-Propyl-P	No growth	1/2000	1/1000	1/500	1/500	1/100
		Growth	...	1/2000(T)	1/1000	1/1000	...
3.	2-Butyl-P	No growth	1/5000	1/5000	1/1000	1/2000	...
		Growth	1/10, 000(T)	1/10, 000	1/2000	1/5000	1/100(T)
4.	2-Hexyl-P	No growth	1/1000	1/1000	...	...	...
		Growth	1/2000(T)	1/2000(T)	1/100	1/100	1/100(T)
5.	2-Heptyl-P	No growth	1/1000	1/1000	...	...	...
		Growth	1/2000	1/2000	1/100	1/100	1/100(T)
6.	2-Decyl-P	No growth	1/1000	1/1000	1/100	1/500	1/100
		Growth	1/2000(T)	1/2000(T)	1/500	1/1000	...
7.	2-Dodecyl-P	No growth	1/2000	1/500	...	1/500	...
		Growth	...	1/1000	1/100	1/1000	1/100(T)
8.	2-Ethyl-F	No growth	1/1000	1/1000	1/100	1/1000	...
		Growth	1/2000	1/2000	1/500	1/2000	1/100(T)
9.	2-Propyl-F	No growth	1/2000	1/500	...	1/1000	...
		Growth	...	1/1000	1/100	1/2000	1/100(T)
10.	2-Butyl-F	No growth	1/5000	1/5000	...	1/5000	...
		Growth	1/10, 000	1/10, 000	1/100(T)	1/10, 000	1/100
11.	2-Pentyl-F	No growth	1/2000	1/1000	...	...	1/100
		Growth	1/5000	1/2000	1/100	1/100	...
12.	2-Hexyl-F	No growth	1/500	1/100	1/100	1/400	1/100
		Growth	1/1000(T)	1/500	1/500	1/500	...
13.	2-Octyl-F	No growth	1/5000	1/5000	...	...	1/100
		Growth	1/10, 000	1/10, 000	1/100	1/100	...
14.	2-Decyl-F	No growth	1/500	1/100	...	...	1/100
		Growth	1/1000(T)	1/500	1/100	1/100	...
15.	2-Dodecyl-F	No growth	1/500	1/1000	...	...	1/100
		Growth	1/1000	1/2000 T)	1/100	1/100	...
16.	P.	No growth	1/1000	1/100	...	...	1/100
		Growth	1/2000	1/500	1/100	1/100	...
17.	F.	No growth	1/500	1/100	...	...	1/100
		Growth	1/1000(T)	1/500	1/100	1/100	...
18.	Phenol	No growth	1/500	1/100	1/1000	1/500	...
		Growth	1/1000	1/500	1/2000	1/1000	...

P = 3-methyl-6-*tert.*-butylphenol. F = 4-*tert*-butyl-6-chlorophenol. T = growth in traces.

Experimental

Evaluation of Bacteriostatic Activity.—The phenols were dispersed in the molten agar medium at about 50° by thorough shaking at a concentration of 1/100. Further dilutions were made from these in the same medium and poured in 3 inch petri dishes in 20 c.c. amounts and immediately placed in a refrigerator for setting. After about an hour these were placed in an incubator at 37° overnight. At the same time sub-cultures of different pathogenic organisms, viz., *S. haemolyticus, S. aureus, P. pyocyaneous, S. typhi* and *B. subtilis* were made on solid media and incubated. Next day suspensions from these sub-cultures were made in normal saline so as to contain approximately thousand million organisms per c.c. From these streak cultures were made on the above nutrient agar containing phenols under test. These were incubated at 37° for 48 hours and the results noted at the end of 24 and 48 hours. If a phenol appeared to be inactive at a certain dilution against most of the bacteria, tests in further dilutions were not carried out. Tests with *B. subtilis* were conducted only with 1/100 dilution and next it was replaced by *S. typhi*. The results are summarised in Table I.

Rideal-Walker Coefficients.—The phenols (0.1 c.c. each, mixed with one drop of Turkey Red oil) were used for preparing various dilutions in distilled water. Three dilutions of each phenol in 10 c.c. aliquots were taken in small Erlenmeyer flasks and placed on water-baths, maintained at 20°, along with carbolic acid in the dilutions 1/115 and 1/120. *S. typhi*, maintained in a standard way, was sub-cultured in the nutrient broth (p_H 7.2) for 24 hours at 37°. It was employed in this test after standardising it with the same broth to contain approximately five hundred million organisms per c.c. Culture suspensions of 0.2 c.c. of *S. typhi* were successively added with a pipette in each of the five flasks with an interval of half a minute. With a standard platinum loop having an internal diameter of 4 mm, transfers were made successively every half a minute in 5 c.c. amounts of ordinary nutrient broth, till four such transfers were made, allowing a maximum contact period of 10 minutes in each dilution of the phenol. Subsequently the test tubes containing the cultured broth were placed in an incubator and the growth of the bacteria was observed after a period of 24 hours. The results are summarised in Table II.

Table II

No.	Phenols.	R.W. coeff.
1.	2-Octyl-4-*tert.*-butyl-6-chloro-phenol	2.6
2.	2-Butyl-4-*tert.*-butyl-6-chloro- ,,	2.6
3.	2-Butyl-3-methyl-6-*tert.*-butyl- ,,	6.5

The authors are thankful to Dr. A. B. Sen for his kind interest in this work.

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Received October 17, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

DETERMINATION OF URANIUM USING DISODIUM 1:8-DIHYDROXY-NAPHTHALENE-3:6-DISULPHONATE (CHROMOTROPIC SALT) AS A COLORIMETRIC REAGENT

By Anil K. Mukherji* and Arun K. Dey

The use of disodium 1:8-dihydroxynaphthalene-3:6-disulphonate (chromotropic salt) as a reagent for the determination of uranium on a micro-scale has been described. The reagent is sensitive to 30 p.p.m. of uranium and Beer's law holds good in the range of concentration of 50-200 p.p.m. The reagent added should be at least 30 times the molar concentration of uranium. The p_H of the medium should be adjusted at 4.00±0.50. For the determination, either a photoelectric colorimeter with a blue filter or a spectrophotometer can be employed. The interference of various cations and anions has also been studied. The chelate has a composition of 1:1 of the reactants.

The determination of uranium on a micro-scale has become an important problem in recent years. Various organic compounds have been suggested as colorimetric reagents, e. g., dibenzoylmethane (Yoe *et al.*, *Anal. Chem.*, 1953, **25**, 1200), salicylic acid (Müller, *Chem. Ztg.*, 1919, **43**, 739) and sulphosalicylic acid (Rodden, "Analytical Chemistry of the Manhattan Project, McGraw Hill Book Co. Inc., New York, 1950). Rây *et al.* (this *Journal*, 1953, **30**, 491) studied the application of salicylamide in the colorimetric estimation of uranium and discussed the relative merits of the common colorimetric procedures of uranium (cf. Rây *et al.*, *Proc. Ind. Sci. Cong.*, 1954, **40**, Part III, p. 48). Rây and Bandyopadhyaya (this *Journal*, 1956, **33**, 21) observed that salicylamidoxime yielded an orange-red complex with uranyl salts and Bandyopadhayaya (*ibid.*, 1956, **33**, 269) employed the spectrophotometric method for working out the details of the use of this reagent in the micro-determination of uranium. The latter author also noted the interference of various common ions on the sensitivity of the colour formation.

In recent communications from this laboratory, a detailed search has been reported for new colorimetric reagents in inorganic analysis. Mukherji and Dey tried Alizarin Red S (this *Journal*, 1957, **34**, 461 ; *Proc. Nat. Acad. Sci., India*, 1957, **26A**, 20), Aluminon (*Z. anal. Chem.*, 1956, **152**, 424), rhodizonic acid (*Chim. Anal.*, 1957, **39**, 148) and Quinalizarin (*Z. anal. Chem.*, 1957, **154**, 347) and suggested further applications of these reagents in colorimetric analysis. They also examined the possibility of using these reagents for the spectrophotometric determination of uranium on a micro-scale (Mukherji and Dey, *Proc. Ind. Sci Cong.*, 1957, **44**, Part III, p. 70).

Disodium 1:8-dihydroxynaphthalene-3:6-disulphonate (chromotropic salt) is known to yield coloured lakes with various metals. Mathur and Dey (*Z. anal. Chem.*, 1957, **154**, 347) have recently reported the reagent to be very sensitive to $Hg\text{-}Hg^{II}$, Sn^{IV}, Au^{III}, Mo^{VI}, Fe^{III} and UO_2^{II} as well. Ware (U. S. Atomic Energy Comm. Rep., *MDDC*, 1945, p. 1432) suggested the use of this reagent for the determination of uranium. As not much work appears to be on record regarding the use of chromotropic salt in colorimetric analysis, it has been thought of interest to investigate the possibility of using this reagent in analysis.

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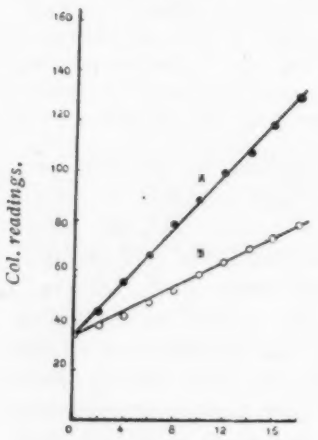
EXPERIMENTAL

Validity of Beer's Law.—Confirmity of the system to Beer's law was investigated as usual using Klett-Summerson's photoelectric colorimeter, and the system was found to obey Beer's law in the range of concentration 50-200 p.p.m, when the reagent added was at least 30-50 times that of the molar concentration of the metallic ion. Some of the typical results are shown in Fig. 1.

FIG. 1



Curve A:

Conc. of uranyl sulphate = 0.0004*M*.

Conc. of chromotropic salt = 0.0100*M*.

Vol. of the reagent taken = 10 c.c.

Total volume = 50 c.c.

Filter used = 42 blue (400-450mμ).

Curve B:

Conc. of uranyl sulphate = 0.0002*M*.

Other conditions same as in curve A.

Stability of the Colour at Room Temperature.—The colour was stable at room temperature. A solution of 0.0002*M* in UO_2^{2+} and 0.0004*M* chromotropic salt at p_H 4.0 gave exactly the same optical density of 0.55 per cm at 400 mμ even after 72 hours' standing at room temperature. The optical densities were determined, using a Unicam SP 500 spectrophotometer.

Influence of Temperature.—The colour intensity was found to decrease beyond 30° as may be seen below.

TABLE I

Uranyl sulphate = 0.0002 *M*. Chromotropic salt = 0.0004 *M*. p_H = 4.0.

Temp.	20°	25°	30°	35°	40°	45°
Optical density/cm (400 mμ)	0.550	0.550	0.550	0.540	0.535	0.530

Influence of p_H.—The colour was found to be stable between p_H 3.50 and 4.80 as shown below.

TABLE II

Temp. 25°. Conc. of uranyl sulphate and of chromotropic salt, same as in Table I.

p_H ...	2.60	3.00	3.50	4.20	4.80	6.30
Opt. density/cm (400 mμ) ...	0.300	0.450	0.550	0.550	0.550	0.700

Sensitivity.—The smallest amount of uranyl ion that can be detected by the reagent is 30 p.p.m.

Influence of Foreign Ions.—The effect of various cations and anions was studied and their approximate tolerance limit determined. The latter denotes the maximum permissible concentration of the foreign ion in the solution under investigation, which would affect the optical density by less then ± 2%. The results are recorded in Table III.

TABLE III

Uranyl sulphate = 0.00002*M* (540 p.p.m.). Chromotropic salt = 0.00040 *M*.
p_H = 4.0 ± 0.50. Temp. = 25°.

Ion.	Added as.	Conc. of ion. (p.p.m.)	Obs. change in opt. density (%).	Tolerance limit. (p.p.m.).
Ag^+	$AgNO_3$	107	+10	
		11	+1	11
Tl^+	Tl_2SO_4	102	−3.5	
		51	−1.5	51
Pb^{2+}	$Pb(NO_3)_2$	207	+6	
		35	+1	35
Hg^+	$Hg_2(NO_3)_2$	...	Interference at all concentrations	0
Hg^{2+}	$HgCl_2$	200	+3	
		75	+1	75
Bi^{3+}	Bi oxalate	80	Turbid	...
Cu^{2+}	$CuSO_4$	126	+6	
		21	+1	21
Cd^{2+}	$CdCl_2$	224	+4	
		112	+2	Large excess
AsO_3^{3-}	H_3AsO_3	123	−0.5	Do.
Sb^{3+}	$Sb_2(SO_4)_3$	76	Turbid	...
Sn^{4+}	$SnCl_4$	...	Interference at all concentrations	0
Fe^{3+}	$FeCl_3$	...	" "	0
Fe^{3+}	Fe amm. sulph.	110	+4	
		55	+2	55
Al^{3+}	$Al(NO_3)_3$	78	+3.5	
		39	+1.5	39
Cr^{3+}	$CrCl_3$	52	+4.5	
		10	+1.5	10
Mn^{2+}	$MnSO_4$	108	−3.5	
		54	−1.5	54
Zn^{2+}	$ZnSO_4$	130	+0.5	Large excess
Ni^{2+}	$NiSO_4$	116	+0.5	Do.
Co^{2+}	$CoSO_4$	116	+3.5	
		58	+1.5	58
Ba^{2+}	$BaCl_2$	137	+13	
		10	+1	10
Sr^{2+}	$SrCl_2$	174	+13	
		13	+1	13
Ca^{2+}	$Ca(NO_3)_2$	160	+14	
		10	+1	10
Mg^{2+}	$MgSO_4$	96	+0.5	Large excess
Be^{2+}	$BeSO_4$	36	+1.5	36
Th^{4+}	$ThCl_4$	232	+3	
		116	+1.5	Large excess
Ce^{3+}	Cerous amm. sulph.	140	+3	
		70	+1.5	70

TABLE III (contd.)

Ion.	Added as.	Conc. of ion. (p.p.m.).	Obs. change in opt. density (%).	Tolerance limit. (p.p.m.).
Ce^{4+}	Ceric sulphate.	140	+4	
		60	+1.5	60
WO_4^{2-}	Na_2WO_4	124	−6	
		50	−1	50
MoO_4^{2-}	$(NH_4)_2MoO_4$	...	Interferes at all concns.	0
VO_3^-	NH_4VO_3	...	" "	0
Zr^{4+}	$ZrO(NO_3)_2$	91	+0.5	Large excess
Ti^{4+}	KTi oxalate	...	Interferes at all concns.	0
SeO_4^{2-}	K_2SeO_4	143	+0.5	Large excess
TeO_3^{2-}	K_2TeO_3	...	Interferes at all concns.	0
CO_3^{2-}	Na_2CO_3	...	" "	0
SO_4^{2-}	K_2SO_4	192	+0.5	Large excess
Cl^-	KCl	70	+3.5	
		35	+1.5	35
Br^-	KBr	160	−0.5	Large excess
I^-	KI	126	−0.5	" "
ClO_3^-	$KClO_3$	83	−0.5	" "
BrO_3^-	$KBrO_3$	128	−0.5	" "
IO_3^-	KIO_3	175	+3.5	
		87	+1.5	87
F^-	NaF	...	Interferes at all concns.	0
SiO_3^{2-}	Na_2SiO_3	154	+6	
		26	+1	26
Citrate	Na citrate	120	−16	
		7	−1	7
Tartrate	K tartrate	130	−10	
		13	−1	13
Oxalate	Amm. oxalate.	94	−8	
		10	−1.5	10
NO_3^-	KNO_3	124	−0.5	Large excess
CNS^-	KCNS	116	−0.5	" "
PO_4^{3-}	Na_2HPO_4	190	−15	
		13	−1.5	13
$S_2O_8^{2-}$	$K_2S_2O_8$	192	−3.5	
		96	−1.5	Large excess
HCO_3^-	$KHCO_3$	...	Interferes at all concns.	0
$S_2O_3^{2-}$	$Na_2S_2O_3$	112	+3.5	
		56	+1.5	56
Acetate	Na acetate	...	Interferes at all concns.	0
$B_4O_7^{2-}$	$Na_2B_4O_7$	...	" "	0

Procedure.—From a consideration of the experimental results recorded above, the following procedure for the estimation of uranium by chromotropic salt may be recommended.

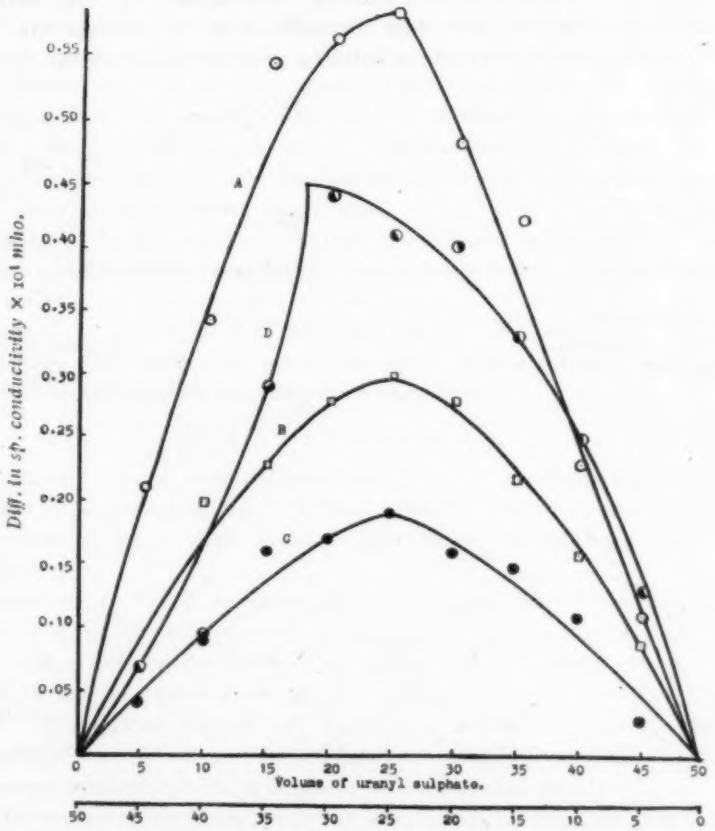
For the determination of uranium in commercial materials, ores, minerals etc., a solution of the sample should be prepared and treated to separate the other elements present as usual (Snell and Snell, "Colorimetric Methods of Analysis", New York, D. Van Nostrand, Vol. I, 1928; Sandell, "Colorimetric Determination of Traces of Metals", 2nd ed., Interscience Publishers, Inc., 1950). The

pure uranyl salt solution as chloride, sulphate or nitrate should be treated directly or in an aliquot portion with an excess (over 25 times the molar proportions of uranium) of a chromotropic salt solution in water. The p_H of the solution should be adjusted at 4.00 ± 0.50. It should then be diluted to the required volume and kept for 15 minutes to attain equilibrium. The optical density can then be read at 400 mμ, using a cell of suitable thickness. The colour intensity can also be measured with a photoelectric colorimeter using an appropriate filter. The temperature of observation should preferably be between 20° and 30°.

Composition of the Coloured Complex.—It was thought to be of interest to determine the composition of the coloured complex formed between uranyl ion and

FIG. 2

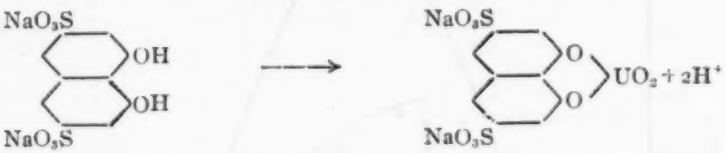
Graphical determination of composition.



Conc. of $UO_2SO_4 = c$. Conc. of chromotropic salt $= c'$. $p = c'/c$. Curve A $c = 0.002M$, $p = 1$. Curve B: $c = 0.001M$, $p = 1$. Curve C: $c = 0.0005M$, $p = 1$. Curve D: $c = 0.002M$, $p = 0.5$.

disodium 1:8-dihydroxynaphtahlene-3:6-disulphonate. Electrical conductance measurements were made with mixtures prepared according to Job's method of continuous variation (*Compt. rend.*, 1925, **180**, 928; *Ann. chim.*, 1928, *x*, **9**, 113). The measurements were carried out using a conductivity cell of the dip type, having a cell constant of 0.132. The bridge used was L. & N. Kohlrausch slide wire with an audio-frequency oscillator. The solutions were always freshly prepared in conductivity water and were kept immersed in an electrically operated thermostat, maintaining a temperature of 25°, before and during the experiments. The results are represented graphically in Fig. 2, where the difference in specific conductivity (observed specific conductivity − sum of the conductivities of the constituent solutions) has been plotted against composition of the mixture.

From the curve it is evident that the components are in the ratio of 1:1 in the chelate. It was noted that the observed conductance of the mixture was in every case higher than the sum of the conductances of the components. This is probably due to the liberation of hydrogen ions as a result of chelate formation, thus,



Chelating agent (I). Uranyl chelate (II).

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Received July 5, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

COMPLEX FORMATION OF URANYL ION WITH *o*-CRESOTIC ACID: POTENTIOMETRIC, COLORIMETRIC AND CONDUCTOMETRIC STUDY

By S. C. Tripathi and Satya Prakash

Like salicylic acid, *o*-cresotic acid also forms complex with uranyl ion. The formation of a red-coloured complex containing uranyl and *o*-cresotate in 1 : 1 molar ratio at about p_H 4.5 is demonstrated by the inflection, break and maximum in colorimeter reading at one equivalent of alkali in all the potentiometric, conductometric and colorimetric titration curves of different mixtures of uranyl nitrate and monosodium *o*-cresotate.

Courtois (*Bull. soc. chim.*, 1923, **33**, 176) has shown the formation of a yellow-orange compound $[C_6H_4(OH)CO_2]UO_2$ with salicylic acid. Weinland and Hager (*Z. anorg. Chem.*, 1927, **160**, 193) have prepared many uranyl compounds with salicylic acid and bases. St. Weil and St. Rozenblum (*Bull. Trans. Inst. Pharm.*, Poland, 1902, **1**, 1) obtained uranyl salicylate, $(C_6H_4.OH.COO)_2UO_2.H_2O$, from salicylic acid and uranyl acetate in hot aqueous solution in small needles of orange-rose colour. Anderson *et al.* (*J. Amer. Chem. Soc.*, 1949, **71**, 909) have studied the complex formation of uranyl ion with sulphosalicylic acid spectrophotometrically by Job's method (*Ann. chim.*, 1928, *x*, **9**, 113). Singh (D. Phil. Thesis, 1956, Allahabad University) has studied the uranyl sulphosalicylate and uranyl chloromercurisulphosalicylate complexes potentiometrically, conductometrically and colorimetrically.

Repman (*Lab. Prakt.*, U. S. S. R., 1941, **16**, 27) has suggested that disodium salt of 5-cresotic acid reacts with uranyl acetate to form a coloured compound which can be used as an indicator for the analysis of phosphates.

Experimental

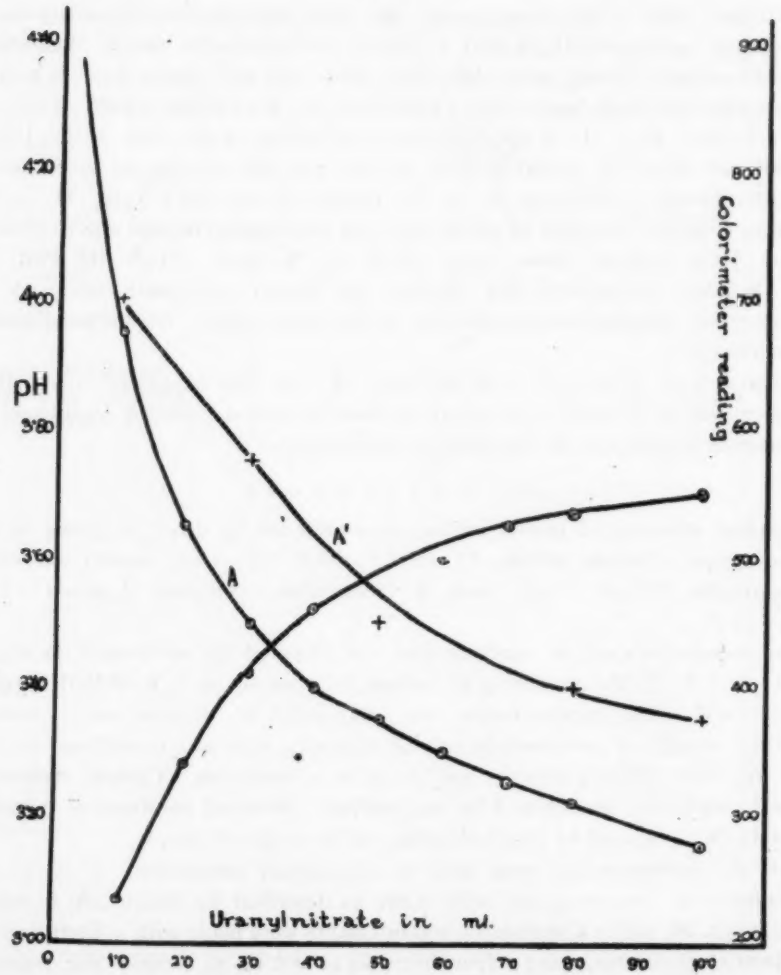
Standard solutions of uranyl nitrate were prepared by direct weighing of Baker's analysed sample of uranyl nitrate, $UO_2(NO_3)_2, 6H_2O$. Uranium content was estimated gravimeatrically (Vogel, "Text Book of Quantitative Inorganic Analysis", London, 1951, p. 471).

The monosodium salt of *o*-cresotic acid was prepared by addition of an equivalent amount of A.R.-E. Merck sample of sodium bicarbonate in L.R.-B.D.H. sample of *o*-cresotic acid. The mother-liquor was evaporated to dryness on a water-bath. The crude sample of monosodium salt of *o*-cresotic acid was crystallised in absolute alcohol in white shining crystals and dried in a desiccator. Carbon, hydrogen and oxygen contents were determined by combustion. Standard solutions of monosodium *o*-cresotate were prepared by direct weighing of the prepared sample.

All the measurements were made at a constant temperature of $32° \pm 0.1°$. p_H and conductivity measurements were made as described by Singh and Prakash (this *Journal*, 1957, **34**, 197). Colorimetric measurements were made with a Klett-Summerson photoelectric colorimeter, using colour filters Ks 42 and Ks 54 within the transmission ranges of 440 – 450 mμ and 500—560 mμ respectively.

Complex-forming Systems.—To study the complex formation of uranyl ion with monosodium *o*-cresotate, the monovariant method was used. To constant volumes of uranyl nitrate varying amounts of monosodium *o*-cresotate were added. Thus, a number of sets of mixtures containing uranyl nitrate and monosodium *o*-cresotate in the ratios 1 : 1, 1 : 2 and 1 : 3 were prepared. To these mixtures varying amounts of standard solutions of caustic soda were added. The total volume of the mixture was kept constant in each case. The sets were left for about 24 hours to attain the equilibrium. For colorimetric measurements, solutions in which precipitation had taken place, were centrifuged to obtain clear solutions.

FIG. 1

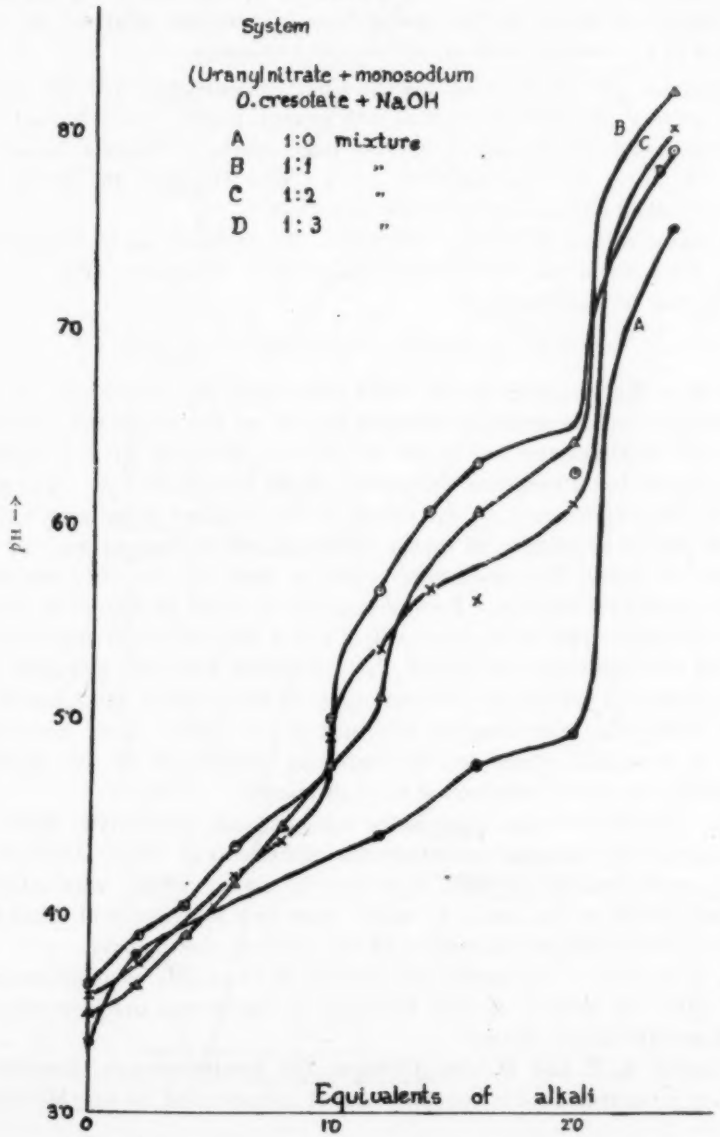


DISCUSSION

In the graph the abscissa represents the number of equivalents of alkali added per gram ion of hydrogen of the ligand, while the ordinate represents the measurements of the physical properties, viz., p_H, sp. conductivity and colorimetric readings.

Fig. 1 represents the changes in hydrogen-ion concentration of monosodium *o*-cresotate by the addition of uranyl nitrate. The p_H of monosodium *o*-cresotate

FIG. 2



(6.8) decreases by the addition of uranyl nitrate and becomes nearly constant after about one equivalent of uranyl nitrate. Curve A′ shows p_H of only uranyl nitrate at similar concentrations. The curve A lies below A′, indicating that there is an increase in hydrogen-ion concentration in the mixtures, which is only possible by the displacement of hydroxyl hydrogen during the complex formation. In Fig. 1, when the colorimetric measurements with filter Ks 42 within the transmission range of 400 – 450 mμ are plotted against the volume of uranyl nitrate, from the curve it is clear that the increase in colour becomes almost constant when one equivalent of uranyl nitrate is added to the monosodium *o*-cresotate solution. It indicates the formation of 1 : 1 complex with uranyl ion and *o*-cresotate.

Fig. 2 shows the variation of hydrogen-ion concentration with the progressive addition of alkali to the systems (*i*) (0.0333*M*) uranyl nitrate (curve A) and mixtures of (0.0333*M*) uranyl nitrate and (0.0333*M*) monosodium *o*-cresotate mixed in the ratios of 1 : 1 (curve B), 1 : 2 (curve C), 1 : 3 (curve D), while the curve E shows the reaction of alkali on monosodium *o*-cresotate itself.

When uranyl nitrate is titrated with alkali, the precipitation of uranyl hydroxide takes place when about two equivalents of alkali have been added (Fig. 1, curve A). The reaction may be represented as :

$$UO_2(NO_3)_2 + 2NaOH \longrightarrow UO_2(OH)_2 + 2NaNO_3$$

Curve E in Fig. 1 represents the blank experiment for comparison. It indicates the variation of p_H of monosodium *o*-cresotate solution on further addition of alkali.

When the two reactants are mixed in 1 : 1, 1 : 2 and 1 : 3 ratios, a reddish white precipitate appears in the mixtures, supernatant liquid being light red. The precipitate dissolves in alkali above p_H 4.15, the colour of the mixture being deep red. Above p_H 6.05, the yellow precipitate of uranyl hydroxide starts precipitating and complete precipitation of uranyl hydroxide takes place at about p_H 8.2 after the addition of about two equivalents of alkali. From the curves B, C and D (Fig. 1) it is clear that there are two inflections in the curves B, C and D (Fig. 2), one at one equivalent and the other at two equivalents of alkali. The displaced hydroxyl hydrogen of monosodium *o*-cresotate is titrated by one equivalent of alkali and a red-coloured complex is formed containing uranyl ion and *o*-cresotate in 1 : 1 ratio. This complex breaks up above p_H 6.05, and uranyl ion is completely precipitated by two equivalents of alkali, denoting the second inflection at two equivalents.

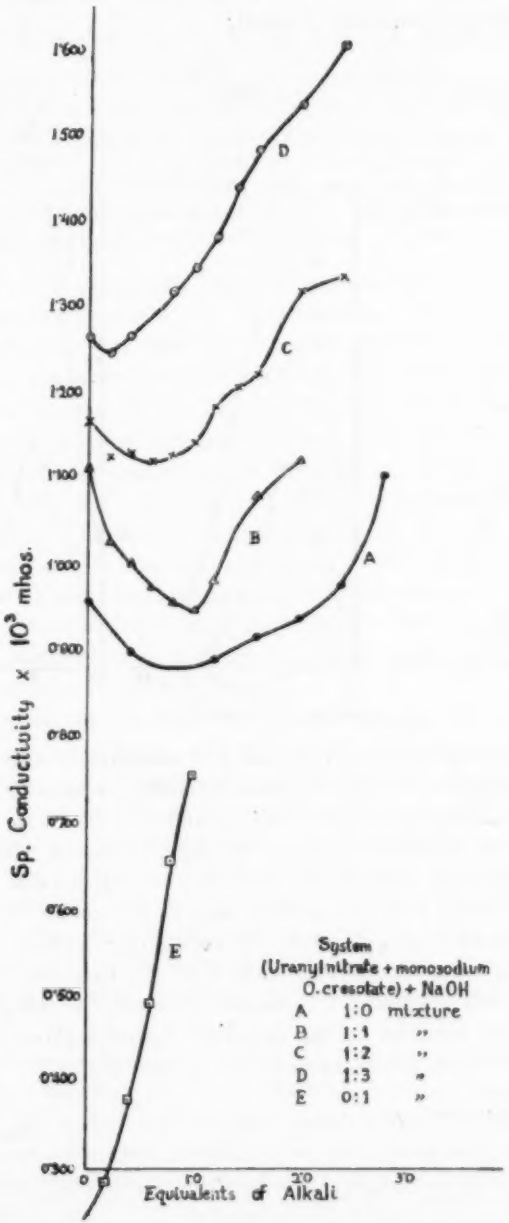
Similar observations were made in the case of specific conductivity study (Fig. 3). Specific conductivity was plotted against the equivalents of alkali. Curve A (Fig. 3) shows the conductometric titration of (0.0333*M*) uranyl nitrate with alkali. There is a definite break in the curve A, when about two equivalents of alkali have been added. The reaction can be represented by the equation, shown above.

Curve E in Fig. 3 represents the reaction of (0.0333*M*) monosodium *o*-cresotate by alkali. Due to absence of free hydrogen in the system and progressive addition of alkali, a straight line is obtained.

The curves B, C and D (Fig. 3) show the conductometric titrations of 1 : 1, 1 : 2 and 1 : 3 mixtures of (0.0333*M*) uranyl nitrate and (0.0333*M*) monosodium

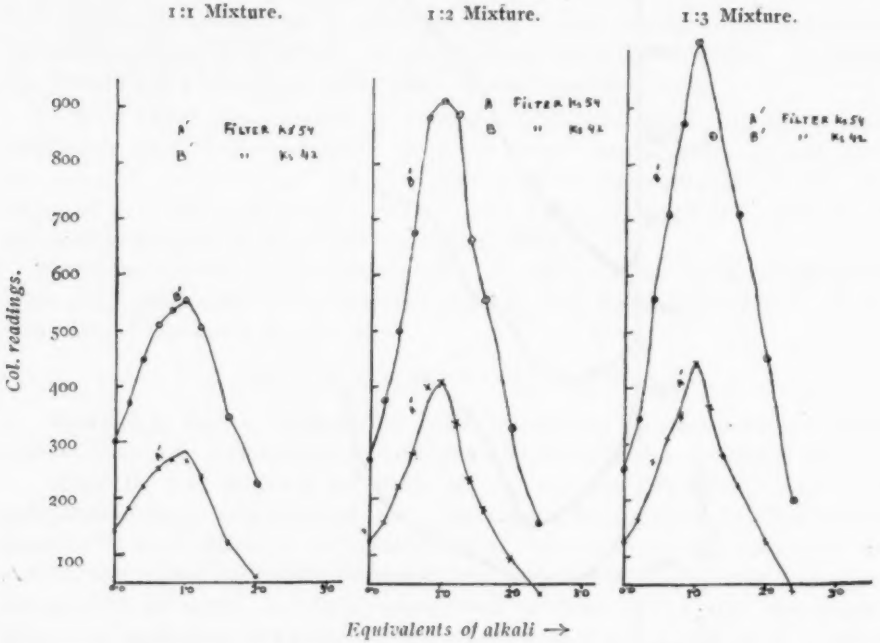
o-cresotate. The curve B shows that specific conductivity decreases by the addition of alkali up to about one equivalent of alkali and then increases showing a break

FIG. 3



at one equivalent. The break at one equivalent of alkali shows the formation of an 1 : 1 complex in which complex formation takes place by oxygen atoms of the hydroxyl and carboxyl groups. Due to an excess of monosodium *o*-cresotate in the system, the specific conductivity curves C and D of 1 : 2 and 1 : 3 mixtures do not show break at exactly one equivalent of alkali.

FIG. 4



Colorimeter readings of 1 : 1, 1 : 2 and 1 : 3 mixtures of (0.0333*M*) uranyl nitrate and (0.0333*M*) monosodium *o*-cresotate show interesting results (Fig. 4). Monosodium *o*-cresotate being colorless gives zero reading and uranyl nitrate also does not show much change on the colorimeter scale. By the addition of alkali the colorimeter readings in all the mixtures increase and reach at a maximum value when one equivalent of alkali is added in all the mixtures at about p_H 4.5, the colour of the solution being dark red. On further addition of alkali, the colorimeter readings decrease and finally uranyl hydroxide is precipitated completely from the complex. This also shows the formation of the above mentioned 1:1 complex of uranyl ion and *o*-cresotate.

The authors are thankful to the Scientific Research Committee, Uttar Pradesh for the award of a research assistantship to one of them (S.C.T.).

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Received February 26, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No 2, 1958]

STUDIES IN CARBOHYDRATES. PART VII. INVESTIGATION OF BAEL FRUIT (*Aegle Marmelos*) MUCILAGE

By V. M. Parikh, T. R. Ingle and B. V. Bhide

The mucilage obtained as a white powder from *Aegle marmelos* has been investigated and found to be non-reducing in character, optically active ($[\alpha]_D^{27}$, +22°) and possessing no acetyl or methoxyl group. It shows positive tests for galactan and pentosan. The hydrolysate of the mucilage shows the presence of galactose, arabinose and a trace of methylpentose. Methylated mucilage on hydrolysis has yielded four sugars, two of which, forming the major part, have been identified as 2 : 3 : 4 : 6-tetra-*O*-methyl- and 4 : 6 di *O*-methyl-D-galactose. Chemical and physical characteristics have been studied with a view to ascertaining the structure of the mucilage.

Aegle marmelos (N. O. Rutaceae), commonly known as *Bael*, is valued in Ayurvedic medicine for dysentery and diarrhoea. A furocoumarin, marmelosin (Dixit and Dutt, this *Journal*, 1932, **9**, 271), has been isolated from the fruit as an active constituent. The present work is concerned with the investigation of the mucilage from the fruit.

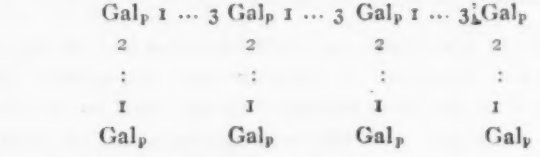
The mucilage is present in the fruits as a jelly, surrounding the seeds, and can be obtained as a white powder by precipitation with alcohol. It is a neutral polysaccharide which does not contain acetyl or methoxyl group (ash, 1.6% ; N, 1%). The mucilage, free from ash and nitrogen, has been obtained as a white powder by the modified procedure of Fraenkel and Jellineks (*Biochem. Z.*, 1927, **185**, 392).

The purified mucilage is non-reducing having $[\alpha]_D^{27}$, +22° (*c*, 2% in water). It gave positive tests for galactan and pentosan and negative tests for ketoses, uronic acid and methylpentoses, though traces of methylpentoses were finally detected in the hydrolysate. The quantitative estimations of sugars gave 84.7% anhydrogalactan, 8.4% anhydropentosan and 2% methylpentosan.

The hydrolysate of the mucilage on chromatographic examination showed the presence of galactose, arabinose, and a trace of methylpentose corresponding to rhamnose. D-Galactose and L-arabinose were obtained in crystalline forms and were characterised by preparation of the usual derivatives. The mother-liquor gave strong tests for rhamnose, but it could not be obtained in a crystalline condition. Mild hydrolysis of the mucilage, under the conditions which have been found to hydrolyse the pentoses in furanose form only (White, *J. Amer. Chem. Soc.*, 1942, **64**, 1507), failed to effect the complete rapture of arabinose from the mucilage, indicating that at least some part of arabinose must be present in the pyranose form.

Methylation of the purified mucilage, initially by dimethyl sulphate and sodium hydroxide and finally by Purdie's reagent, gave a methylated product {OMe, 39.6% ; $[\alpha]_D^{27}$, −41° (*c*, 2% in chloroform}, which on hydrolysis yielded four sugars, two of which have been identified as 2 : 3 : 4 : 6-tetra-*O*-methyl- and 4 : 6-di-*O*-methyl-D-galactose and found in the hydrolysate in approximately equimolecular proportions. The remaining two sugars were not examined as the quantities obtained were too small. However, the chromatographic studies indicate that at least one of them is an arabinose derivative.

The molecular weight of the purified mucilage was found to be 1364 (cryoscopically). This low molecular weight suggests that the methylpentose (2%) present may not probably be the constituent of the polysaccharide molecule. A molecule of the mucilage might be composed of 8 units of D-galactose and 1 unit of L-arabinose which requires 89.6% anhydrogalactan (found 84.7%) and 8.13% anhydropentosan (found 8.4%). Although the data cited in the present work do not lead to a definite structure of the mucilage due to the non-identification of arabinose derivative, it is evident from the relative proportion of galactose molecule and its derivatives that the mucilage is highly branched and possesses 1:2 and 1:3 linkages. The optical rotations of the mucilage and of its methylated derivative suggest β linkages. One out of several structures satisfying the above results is shown below.



Gal$_p$ = D-galactopyranose.
(The position of arabinose unit is not decided.)

The results of the periodate oxidation are also in agreement with this type of structure.

EXPERIMENTAL

Isolation of the Mucilage and Purification.—The fruits (20), each weighing on an avarage 400 g., were cut open in the middle and seeds encapped in the cavities were collected along with the mucilaginous coating. The jelly (500 c.c.) with the seeds was diluted with water (100 c.c.) and pressed through muslin. The filtrate was gradually added to ethanol (90%, 1.5 litres) when the mucilage precipitated as a sticky mass. On trituration with absolute alcohol, it formed a granular powder (yield 270 g.). The dry powder gave 1.6% ash which dissolved completely in dilute hydrochloric acid and showed the presence of Fe^{3+}, Ca^{2+} and PO_4^{3-}. It contained 1.1% nitrogen and did not show the presence of acetyl and methoxyl groups.

An aqueous solution of the mucilage, under the microscope, was found to be heterogeneous containing insoluble particles, the number of which was considerably lowered after filtering the solution hree ttimes (found: N, 0.6%). The mucilage, free from nitrogen and ash, was obtained by the following procedure. The mucilage (10 g.), dissolved in water (50 c.c.), was heated on a water-bath with barium hydroxide (5%, 50 c.c.) for 4 hours and then neutralised with requisite amount of sulphuric acid, and CO_2 was passed to precipitate the residual barium. The solution was filtered and the mucilage was precipitated by adding the filtrate to alcohol containing 1% HCl (1 litre). The precipitate was dissolved in water and reprecipitated by alcohol. Two to three similar treatments gave the mucilage as an amorphous powder. It was washed with ethyl alcohol till free from Cl^- (ash, negligible ; N, nil).

The mucilage gave tests for galactan and pentosan and did not answer the tests for ketoses, uronic acid and methylpentoses, though the traces of methylpentoses were detected later. Pentoses and methylpentoses were estimated by A. O. A. C. methods, while galactose was estimated by hydrolysing the mucilage and preparing the galactose α-methylphenylhydrazone according to Hirst, Jones and Woods (*J. Chem. Soc.*, 1947, 1048). The results of the estimation are given above. The molecular weight of the mucilage was found to be 1364 cryoscopically.

Hydrolysis of the Mucilage by 10% H_2SO_4.—The mucilage (10 g.) was dissolved in 10% H_2SO_4 (100 c.c.) and heated to 90°. The hydrolysis was followed polarimetrically as well as by finding the reducing power of the hydrolysate by Bertrand and Mohr's method, calculated as glucose. The reducing power and the rotations are given below.

TABLE I

Period (in hrs.)	0	1	2	3	4	5
$[\alpha]_D^{27}$	...	+69°.5	+82°	+91°.5	+95°	+95°
Reducing power of the hydrolysate	Nil	49.6	62	89.2	94.3	94.3

The hydrolysate on neutralisation with barium carbonate was concentrated to a syrup which on chromatographic examination was found to contain three reducing sugars. The syrup on extraction with dry methanol left a residue (A), which was mainly galactose ; the methanolic extract (B) was chromatographically found to contain arabinose and a methylpentose, probably rhamnose. The residue (A) on crystallisation gave pure crystalline D-galactose, m.p. and mixed m.p. 164° ; $[\alpha]_D^{28}$, +80° (*c*, 2% in water). Its α-methylphenylhydrazone melted at 186°. The filtrate (B) on concentration gave white crystals of L-arabinose which were removed and purified by recrystallisation, m.p. and mixed m.p. 158° ; $[\alpha]_D^{28}$, +105° (*c*, 2% in water). It gave a diphenylhydrazone, m.p. 201°. From the mother-liquor, rhamnose could not be obtained in a crystalline form ; however, the mother-liquor gave positive Rosenthaler's test and the R_f value of the methylpentose present was identical with that of rhamnose.

Isolation of Galactan.—The mucilage (20 g.) was heated at 90° with 0.1*N*-H_2SO_4 (200 c.c.). The mixture became slightly reducing after 8 hours. The heating was continued and the reducing power estimated after 4 hours. It was found that the reducing power of the hydrolysate remained more or less constant after 24 hours. After hydrolysing the mucilage for 32 hours, the acid was neutralised by barium carbonate and the filtrate was added to ethanol (1.5 litres), when the degraded mucilage precipitated as a white solid. The chromatographic examination of the alcoholic extract showed the presence of galactose, arabinose and rhamnose. The degraded mucilage was freed of monosaccharides and was again hydrolysed, when galactose and arabinose were detected in the hydrolysate, indicating that the arabinose present in the mucilage was in the pyranose form.

Methylation of the Mucilage.—The mucilage (20 g.) was methylated 4 times at 30°, by adding dimethyl sulphate (300 c.c.) and NaOH (850 c.c., 30%) each time

during 7 hours and concentrating the solution to remove sodium sulphate. The partially methylated mucilage was dissolved in acetone and remethylated 3 times by the above procedure. The partially methylated product was dissolved in chloroform, washed with 20% sodium sulphate solution and was finally dried over anhydrous sodium sulphate. The extract on removal of the solvent yielded a solid (19 g., OMe, 32%). It was further methylated twice by Purdie's reagent (*J. Chem Soc.*, 1903, **83**, 1021) (found : OMe, 37.9%). Further treatment with Purdie's reagent did not increase the methoxyl content ; yield 17.5 g.

Fractionation of the Methylated Mucilage.—The methylated mucilage was fractionated in chloroform-petroleum ether (b.p. 60-80°) solvent system. The product was dissolved in chloroform and fractionally precipitated by adding petroleum ether. Four different fractions were collected (Table II).

TABLE II

Fraction No.	%OMe.	$[\alpha]^{27}_{D}$. ($c = 2\%$ in $CHCl_3$).	Yield.
I	35.0	−38°.1	2.1 g.
II	36.6	−38°.3	6.0
III	37.0	−39°.0	6.2
IV	39.6	−41°.1	2.3

All these fractions on hydrolysis gave the same pattern of reducing sugars on paper chromatograms ; hence fraction IV was only examined further.

Hydrolysis of Fraction (IV).—Fraction IV (0.5 g.) was heated with 7% HCl-MeOH mixture (60 c.c.) in a sealed tube for 6 hours at 90°. It was then diluted with *N*-HCl (60 c.c.) and heated further for 3 hours. The hydrolysate was treated with silver carbonate, filtered and the filtrate was treated with hydrogen sulphide to remove silver ions, and again filtered. The filtrate on concentration under reduced pressure gave a syrup (0.45 g.) which showed the presence of four sugars on paper chromatograms. The syrup (0.4 g.) was separated on the cellulose column (60 × 5 cm) using benzene-ethanol-water (169 : 47 : 15; v/v ; 1200 c.c.) as the eluting mixture. Fractions IV_A, IV_B, IV_C and IV_D were collected out of which IV_A and IV_D formed the major part of the syrup (about 80 to 85%), while IV_B and IV_C were in small quantities and were not examined.

Fraction IV_A : *Identification of* 2 : 3 : 4 : 6-*Tetra*-*O*-*methyl*-D-*galactose*.—The syrup had OMe, 46.96% ; $[\alpha]^{27}_{D}$, +60°.1 (*c*, 2% in ethanol). On a paper chromatogram it ran side by side with the authentic specimen of 2 : 3 : 4 : 6-tetra-*O* methyl-D-galactose ($C_{10}H_{20}O_6$) which requires Me, 52.1% ; $[\alpha]^{27}_{D}$, +62°.6 (ethanol) (Irvine and Cameron, *J. Chem. Soc.*, 1904, **85**, 1071), concluding that fraction IV_A (yield 0.18 g.) was 2 : 3 : 4 : 6-tetra-*O*-methyl-D-galactose. It was further confirmed by preparing its anilide, m.p. and mixed m.p. 194°. (Found : OMe, 39.6. $C_{16}H_{25}O_5N$ requires OMe, 39.9%).

Fraction IV_b: *Identification of* 4:6-*Di*-O-*methyl*-D-*galactose*.—This syrup, on trituration with dry ether, gave white crystals (yield 0.16 g.), m.p. 161° ; OMe (found) 41.6% ; $[\alpha]_D^{27}$, +97°.5 (*c*, 0.48% in water). It did not reduce Fehling's solution, indicating that the glycoside was formed during separation. It was further hydrolysed by 1*N*-HCl for 3 hours and worked up as described under the hydrolysis of fraction IV. The syrup, thus obtained, was reducing and it was crystallised from benzene-ethanol-water, m.p. 103° ; OMe, 27% ; $[\alpha]_D^{27}$, +110° (*c*, 0.36% in water). The physical constants suggested that the sugar might be 2:4 di-*O*-methyl-D-galactose monohydrate ($C_8H_{16}O_6.H_2O$) which requires OMe, 27.4% ; $[\alpha]_D^{27}$, + 123° falling to +82° and m.p. 105° (Hirst and Jones, *J. Chem. Soc.*, 1939, 1482). The crystalline sugar gave an anilide, m. p. 206° ; OMe, 22.2% ; N, 5.3% ; $[\alpha]_D^{27}$, −169°.5 (*c*, 0.36% in pyridine) which confirmed the above inference as 2:4-di-*O*-methyl-D-galactose anilide ($C_{14}H_{21}O_5N$) which requires OMe, 21.9% ; N, 5.0% and possesses m.p. 207° ; $[\alpha]_D^{30}$, −174° (*c*, 0.35% in pyridine) (Hirst and Jones, *loc. cit.*).

Periodate Oxidation of the Mucilage.—The dry mucilage (0.4614 g.) was dissolved in distilled water (65 c.c.) and sodium metaperiodate (35 c.c., 0.2*M*) was added to it. The oxidation was carried out for 16 hours when it was found to be complete. The mucilage (360 g.) consumed two molecules of sodium metaperiodate and liberated one molecule of formic acid.

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Received October 16, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

SYNTHESIS IN DIHALOGENATED 5-AMINOACRIDINE SERIES

By A. G. Munshi*, P. M. Dholkia and K. S. Nargund

5 *N*-substituted amino-2:3-dichloro-7-methoxy- and the corresponding demethoxy-acridine derivatives have been described.

Atabrine, the well-known antimalarial, is 2-chloro-7-methoxy-5-(4-diethylamino-1-methylbutyl)amino-acridine dihydrochloride. It has been established that chlorine is more effective in endowing antimalarial properties in acridine derivatives than the methoxy group. Moreover, 1-chloro-, 2-chloro- and 3-chloro-5-(4-diethylamino-1-methylbutyl)amino-acridines were reported as active with quinine equivalent as 0.8, 4.0 and 0.6 respectively (Wiselogle, "Survey of Antimalarial Drugs", 1941-45, Vol. II, Part II, pp. 1930-31).

With a view to studying the effect of an additional chlorine atom on the antimalarial properties of atabrine, dialkylamino-alkylamino derivatives of 2:3-dichloro-7-methoxy-acridine and the corresponding demethoxy-acridine diervatives have been synthesised.

3′:4′-Dichloro- and 3′:4′-dichloro-4-methoxy-diphenylamine-2-carboxylic acids, required for the synthesis of 2:3-dichloro- and 2:3-dichloro-7-methoxy-5-(4-diethylamino-1-methylbutyl)aminoacridines, were obtained by Ullmann's condensation (*Ber.*, 1905, **38**, 2156) of 3:4-dichloroaniline with *o*-chlorobenzoic acid and 6-bromo-3-methoxybenzoic acid respectively. The above-mentioned acids on cyclisation with an excess of phosphorus oxychloride afforded the mixture of two isomeric 5-chloroacridines, viz., 2:3:5-trichloro- and 3:4:5-trichloro-7-methoxyacridines which were separated by repeated fractional crystallisation from toluene, followed by acetone.

Usually it is found that 5-chloroacridine, obtained by *para*-closure, has a higher melting point than the 5 chloroacridine obtained by *ortho*-closure (Albert and Linnell, *J. Chem. Soc.*, 1936, 88; Lehmstedt and Schrader, *Ber.*, 1937, **70**, 838). Therefore the product having higher m.p. (192-93°) may be 2:3:5-trichloro-7-methoxyacridine, while one having lower m.p. (179°) may be 3:4:5-trichloro-7-methoxyacridine. 2:3:5-Trichloro-7-methoxyacridine was prepared by Feldman and Kopeliowitsch (*Arch. Pharm.*, 1935, **273**, 488) by an unambiguous synthesis. They obtained it as an oily product on cyclising 4:5-dichloro-4′-methoxydiphenylamine-2-carboxylic acid and recorded its m.p. as 192-93°. This supports the conclusion which has been drawn above.

The yields of the above-mentioned 5-chloroacridines were very small; and in the case of 3′:4′-dichlorodiphenylamine-2-carboxylic acid, 2:3-dichloroacridone was obtained instead of the expected 5-chloroacridine derivative; the alternative method of preparing substituted 5-aminoacridines through acid chloride was adopted.

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EXPERIMENTAL

3′:4′-Dichloro-4-methoxydiphenylamine-2-carboxylic acid was prepared by refluxing the mixture of 6-bromo-3-methoxybenzoic acid (9 g.), fused potassium carbonate (6 g.), *iso*amyl alcohol (30 c.c.), 3:4-dichloroaniline (7 g.) and copper powder (0.3 g.) for 4 hours at 140°. After removal of amyl alcohol by steam-distillation, the residual liquid was treated with animal charcoal and filtered hot. The solid separating on acidification was crystallised from acetic acid in small green needles, m.p. 187°, yield 6 g. (Found: Cl, 22.9; equiv., 312.0. $C_{14}H_{11}O_3NCl_2$ requires Cl, 22.8%; equiv., 312.0). The *acid chloride* was obtained by refluxing a mixture of the above acid (1 g.), thionyl chloride (3 c.c.) and benzene (10 c.c.) and crystallised from benzene, m.p. 117°. (Found: Cl, 32.6. $C_{14}H_{10}O_2NCl_3$ requires Cl, 32.2%).

2:3:5-Trichloro- and 3:4:5-trichloro-7-methoxyacridines were obtained in the form of a mixture by treating the preceding acid (5 g.) with $POCl_3$ (30 c.c.) at 110-15° for 3 hours. After removing the excess of $POCl_3$ by petrol-ether, the residual insoluble, dark red, sticky liquid was treated with chloroform. The chloroform-extract, after treating it with ice and ammonia, was dried and the chloroform removed by distillation. A green solid was obtained which melted between 157° and 200°. Two isomers were separated by fractional crystallisation from toluene. The first fraction crystallised as a fine yellow solid, m.p. 192°. (Found: Cl, 34.4. $C_{14}H_{16}ONCl_3$ requires Cl, 34.1%). The second fraction was obtained in a pure state after repeated crystallisations from acetone, m.p. 179°. (Found: Cl, 34.3. $C_{14}H_{16}ONCl_3$ requires Cl, 34.1%).

2:3-Dichloro-5-phenoxy-7-methoxyacridine was prepared by refluxing the mixture of 2:3:5-trichloro-7-methoxyacridine (1 g.) and freshly distilled phenol (5 g.) for 3 hours at 120°. When the reaction mixture, after cooling, was poured into 2*N* NaOH solution (30 c.c.), a yellow solid separated which crystallised from acetic acid, m.p. 180°. (Found: Cl, 18.3. $C_{21}H_{14}O_2NCl_2$ requires Cl, 18.1%).

3:4-Dichloro-5-phenoxy-7-methoxyacridine was obtained by refluxing 3:4:5-trichloro-7-methoxyacridine (1 g.) with phenol (5 g.), as mentioned above, m.p. 153°. (Found: Cl, 18.4. $C_{21}H_{14}O_2NCl_2$ requires Cl, 18.1%).

7-Methoxy-2:3-dichloro-5-(4-diethylamino-1-methylbutyl)amino-acridine dihydrochloride was prepared by heating the mixture of the acid chloride of 3′:4′-dichloro-4-methoxydiphenylamine-2-carboxylic acid (1 g.), dry benzene (30 c.c.) and 4-diethylamino-1-methylbutylamine (0.5 g.) for half an hour. $POCl_3$ (3 c.c.) was then added to the reaction mixture and refluxed for 6 hours. After removing benzene, the residue was twice washed with petroleum ether to remove excess of $POCl_3$. The dark red residue was extracted with absolute alcohol, from which a yellow solid separated on adding acetone. It was then purified by redissolving it in absolute alcohol and reprecipitating by acetone. The dried product melted at 237°. (Found: N, 8.0; Cl, 28.2. $C_{23}H_{31}ON_3Cl_4$ requires N, 8.2; Cl, 28.0%).

Other 5-*N*-substituted aminoacridine derivatives have been obtained by following the method described above and they are summarised in Table I.

TABLE I

[AD stands for aminoacridine dihydrochloride]

S. No.	Product.	M.P.	Mol. formula.	% Chlorine. Found.	Calc.
1.	7-Methoxy-2 :3-dichloro-5-(γ-piperidinopropyl)-AD	158°	$C_{21}H_{23}O_2N_3Cl_2$	16.6	16.5
2.	7-Methoxy-2 :3-dichloro-5-(γ-morpholinopropyl)-AD	238°	$C_{22}H_{27}ON_3Cl_4$	29.2	28.9
3.	2 :3-Dichloro-5-(γ-piperidinopropyl)-AD	254°	$C_{21}H_{25}N_3Cl_4$	31.0	30.9
4.	2 :3-Dichloro-5 (4-diethylamino-1-methylbutyl)-AD	248°	$C_{22}H_{29}N_3Cl_4$	29.9 8.73*	29.9 8.8*

* Refers to nitrogen value.

The authors express their grateful thanks to Dr. N. M. Shah for his kind interest and help during the course of this work.

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Received October 18 1957.

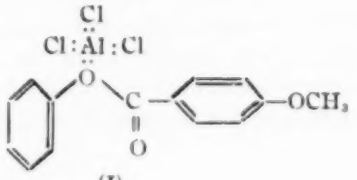
[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

HYDROXYKETONES. PART VIII. THE FRIES REACTION OF THE ESTERS OF ANISIC ACID AND A STUDY OF ITS MECHANISM

By A. R. Gupta and G. S. Saharia

Fries migrations of the esters of anisic acid with phenol and isomeric cresols have been studied. It has been observed that the methoxyl group does not interfere in the reaction and normal migration products are obtained.

During the course of our earlier studies on the mechanism of the Fries reaction (Saharia and Sharma, this *Journal*, 1956, **33**, 788 ; *J. Sci. Ind. Res.*, 1957, **16B**, 125), it was observed that steric factors played an important part and unless the phenoxyl oxygen atom was available to form the complex (I), no migration took place, although the carbonyl group might be sterically free to form the complex. This observation rules out the idea of some workers (Ralston *et al.*, *J. Org. Chem.*, 1940, **5**, 645, 2165 ; 1941, **6**, 751 ; Amin and Shah, *J. Univ. Bombay*, 1948, **17**, 1) that the carbonyl oxygen atom is important for the complex formation in this reaction.



(I)

Another important factor in the Fries migration, worth considering, is the electron density at the phenoxyl oxygen atom. This aspect of the problem arises only when there is another electron donor group competing for the complex formation. The present communication presents a study of the Fries reaction involving the esters of anisic acid. During the earlier work with *m*-methoxybenzoic acid esters (Saharia and Sharma, *loc. cit.*), it was observed that the methoxyl group was preferred for the complex formation though it occurred also at the phenoxyl oxygen atom, while with the esters of *o*-methoxybenzoic acid, steric factors played a major role. Based on the results obtained during the migrations of the esters of anisic acid, it is evident that the electron density at the methoxyl group is insufficient for complex formation, which takes place at the phenoxyl oxygen atom, as normal migration products are obtained.

The study of the Fries migration of the esters of the three isomeric methoxybenzoic acids therefore leads us to the conclusion that the electron density at the phenoxyl oxygen atom and its availability against any steric factors for the complex formation are the necessary requirements for the reaction to proceed ; the carbonyl group does not play any important part in this migration. During the

present work the Fries reactions were studied at 120° and 160°, and it was observed that temperature had little effect on the course of the reaction though comparable yields of the hydroxyketones were obtained in some cases at the two temperatures.

An important observation made during the course of this study was the non-formation of the *o*-hydroxyketones even at 160° ; phenyl anisate, when migrated at 160°, afforded negligibly small traces of the *ortho*-ketone, which could not be isolated inspite of repeated efforts. However, *m*- and *p*-cresyl anisates gave exclusively the *o*-hydroxyketones at 120° and 160°.

Phenyl anisate alone gave the demethylated ketone at 160°, while in no other case demethylation was observed.

The hydroxyketones were characterised through their 2:4-dinitrophenylhydrazones.

EXPERIMENTAL

Anisic acid, required for this work, was prepared in good yields from *p*-hydroxybenzoic acid by the method of Kalff and Robinson (*J. Chem. Soc.*, 1925, 1970) and was then converted into anisoyl chloride by refluxing with thionyl chloride. The esters of phenol and isomeric cresols were prepared by the Schotten-Baumann reaction.

The Fries migration of these esters was carried out using 1.3 moles of anhydrous aluminium chloride for one mole of the ester in absence of any solvent at 120° and 160°, and the reaction products worked up in the customary manner. It was observed that at the lower temperature, the yields of the hydroxyketones were slightly better and that some free anisic acid was recovered in most of the cases.

TABLE I

Esters.	
I. Phenyl anisate :	Colorless needles from dilute ethanol, m.p. 75-76° (lit. 76°).
II. *o*-Cresyl anisate :	Colorless needles from dilute ethanol m.p. 65°. (Found : C, 73.9 ; H, 5 3 ; $C_{15}H_{14}O_3$ requires C, 74.4 ; H, 5.8%).
III. *m*-Cresyl anisate :	Colorless plates from dilute ethanol m.p. 60°. (Found : C, 71.6 ; H, 6.1 ; $C_{15}H_{14}O_3$, $1/2H_2O$ requires C, 71.7 ; H, 6.0%).
IV. *p*-Cresyl anisate :	Colorless plates from dilute ethanol, m.p. 67°. (Found : C, 74.5 ; H ; 5.8 , $C_{15}H_{14}O_3$ requires C, 74.4 ; H, 5 8%).

Hydroxyketones

1. Phenyl anisate (I) gave two ketones (*a* & *b*) at 160°, which were separated by their solubility difference in benzene, and only one (*a*) at 120°.

(*a*). *4-Hydroxy-4′-methoxybenzophenone* was crystallised from benzene in needles, m.p. 150-51° (lit. 151°).

(*b*). *4 : 4′-Dihydroxybenzophenone* was obtained in small yields and crystallised from ethanol in needles, m.p. 206-207° (lit. 205-207°).

2. The ester (II) gave *3-methyl-4-hydroxy-4'-methoxybenzophenone*, which was crystallised from dilute ethanol in orange needles, m.p. 186°. (Found: C, 73.8; H, 5.3. $C_{15}H_{14}O_3$ requires C, 74.4; H, 5.8%). Its 2:4-dinitrophenylhydrazone had m. p. 221-2°.

3. The ester (III) gave *2-hydroxy-4-methyl-4'-methoxybenzophenone*, which on crystallisation from ethanol in lustrous needles had m.p. 96-97°. (Found: C, 74.6; H, 6.5. $C_{15}H_{14}O_3$ requires C, 74.4; H, 5.8%).

It gave a violet coloration with ferric chloride and its 2:4-dinitrophenylhydrazone had m.p. 198-200°.

4. The ester (IV) furnished *2-hydroxy-5-methyl-4'-methoxybenzophenone*; it was crystallised from petroleum ether in colorless plates, m.p. 108-109° (lit. m.p. 108-109°).

It gave a violet coloration with ferric chloride and its 2:4-dinitrophenylhydrazone had m.p. 208-209°.

Thanks are due to Dr. V. V. S. Murty for the microanalyses.

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Received July 6, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

SYNTHESIS OF SUBSTITUTED AROYLBENOFURANS. PART I

By A. B. Sen and M. S. Saxena

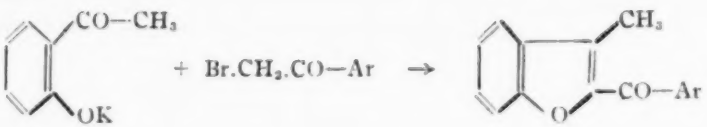
Several chloro-aroylbenzofurans have been synthesised by the Rap reaction, using *o*-hydroxyketones.

Several aroylbenzofurans were prepared by Schraufstätter and Deutsch (*Z. Naturforsch.*, 1949, **46**, 276) for their therapeutic evaluation. Closely related heterocycles of the type of *iso*flavenes and *iso*flavons have been observed by Bradbury and White (*J. Chem. Soc.*, 1951, 3447 ; 1953, 871) to possess estrogenic activity. Coumarins also have been found to possess estrogenic activity by Gley and Mentzer (*Compt. rend. Soc. Biol.*, 1945, **139**, 1055).

These investigations and the close similarity among *iso*flavens, *iso*flavones, coumarins and the benzofurans, led Bisagni, Buu Hoï and Royer (*J. Chem. Soc.*, 1955, 3688, 3693) to synthesise a number of 2-aroylbenzofurans and related compounds, and some of these compounds showed estrogenic activity.

The present investigation was therefore undertaken to synthesise a number of chloro-aroylbenzofurans, with a view to studying their therapeutic value.

The method used for the preparation of the 2-aroylbenzofurans is that of Rap (*Gazzetta*, 1895, **25**, 285), where the potassium salt of a suitably substituted *o*-hydroxyketone is condensed with a substituted bromoacetophenone. The reaction can be represented as :



The easy availability of the *o*-hydroxyketones through the Fries rearrangement of phenolic esters, and the comparative ease with which the Rap reaction could be effected, led us to follow the same synthesis. The *o*-hydroxyketones were obtained by the Fries rearrangement of acetates, propionates and butyrates of *o* chloro- and 2 : 4-dichlorophenols. The esters were obtained in over 90% yield by using the method of Chattaway (*J. Chem. Soc.*, 1931, 2495) and were pure enough for the Fries migration. The Fries rearrangement of the acetate, propionate and butyrate of 2 : 4-dichlorophenol has already been reported in the literature (Chien and Yin, *Chem. Abs.*, 1940, **34**, 1979), whereas the rearrangement of the corresponding esters of *o*-chlorophenol has been effected for the first time.

Phenacyl bromide and *p*-chlorophenacyl bromide, required in the synthesis, were obtained by the bromination of acetophenone and *p*-chloroacetophenone respectively, in glacial acetic acid (Reid, *J. Amer. Chem. Soc.*, 1919, **41**, 77).

The 2-aroylbenzofurans were characterised through their oximes, excepting in the case of 3-methyl-7-chloro-2-*p*-chlorobenzoyl-benzofuran, which was characterised through its semicarbazone.

TABLE I

S. No.	Benzofuran.	M.P.	% Carbon.		% Hydrogen.		Colour developed		Oxime		
			Found.	Calc.	Found.	Calc.	Benzofuran & conc. H_2SO_4.		M.P.	Found.	Calc.
A.	3-Methyl-5 :7-dichloro-2-benzoyl-	140°	62.26	62.94	3.27	3.28	Deep brown	yellow	168°	C :59.60 H : 3.40 N : 4.20	60.00% 3.44 4.38
B.	3-Methyl-5 :7-dichloro-2-*p*-chloro-benzoyl-	218°	56.02	56.56	2.61	2.65	Reddish brown	yellow	195°	C :53.85 H : 2.41 N : 3.80	54 16 2.82 3.95
C.	3-Ethyl-5 :7-dichloro-2-benzoyl-	90°	63.24	63.84	3.34	3.76	Yellow		137°	C :60.76 H : 3.24 N : 4.20	61.08 3.89 4.13
D.	3-Ethyl-3 :7-dichloro-2-*p*-chloro-benzoyl-	135°	57.01	57.7	2.92	3.11	Red	yellow	162°	C :54.76 H : 3.11 N : 3.65	55.36 3.26 3.80
E.	3-Propyl-5 :7-dichloro-2-benzoyl-	93°	64.12	64.87	4.11	4.20	Red	yellow	130°	C :61.95 H : 4.29 N : 4.12	62.07 4.31 4.02
F.	3-Propyl-5 :7-dichloro-2-*p*-chloro-benzoyl-	135°	58.15	58.78	3.26	3.54	Red	yellow	160°	C :56.20 H : 3.01 N : 3.64	56.46 3.66 3.66
G.	3-Methyl-7-chloro-2-benzoyl-	110°	69.92	70.98	3.92	4.06	Deep reddish	brown	157°	C :67.02 H : 4.02 N : 4.85	67.24 4.21 4.90
H.	3-Methyl-7-chloro-2-*p*-chloro-benzoyl-	140°	62.20	62.94	3.25	3.28	Very dark reddish	brown	190°*	C :55.89* H : 3.23* N :11.45*	56.35* 3.59* 11.60*
I.	3-Ethyl-7-chloro-2-benzoyl-	80°	71.20	71.70	4.20	4.57	Orange	yellow	134°	C :67.75 H : 4.15 N : 4.63	68.11 4.67 4.47
J.	3-Ethyl-7-chloro-2-*p*-chloro-benzoyl-	114°	63.11	63.94	3.41	3.76	Red	yellow	147°	C :60.82 H : 3.34 N : 4.21	61.08 3.89 4.19
K.	3-Propyl-7-chloro-2-benzoyl-	82°	69.98	72.38	5.01	5.02	Yellow		145°	C :68.27 H : 5.01 N : 4.09	68.91 5.10 3.11
L.	3-Propyl-7-chloro-2-*p*-chloro-benzoyl-	130°	64.23	64.87	4.01	4.20	Violet	yellow	151°	C :61.73 H : 4.11 N : 3.61	62 07 4.31 3.35

* Of semicarbazone.

Some of the benzofurans, prepared by Buu Hoï *et al* (*loc. cit.*) have been found to give a red halochromy with concentrated sulphuric acid. Most of the compounds reported in this paper have also responded to this test.

EXPERIMENTA

Preparation of the Esters.—The phenol (1 mole) was dissolved in NaOH solution (1.5 moles, 50 c.c.) and mixed with crushed ice (600 g.) and cooled externally by ice. The appropriate acid anhydride (1.25 moles) (acetic, propionic or butyric) was quickly added and the mixture vigorously shaken for a few seconds. After separation of the ester a 10% NaOH solution (20 c.c.) was added and shaken again. It was extracted with ether, the ether extract was washed first with dilute caustic soda, then with water, dried over anhydrous calcium chloride and the ether removed. The yields in the case of 2 : 4-dichloro- and *o*-chloro-phenyl butyrate were nearly 100%. In all other cases it was over 90%. The esters were used directly for the Fries rearrangement.

2-*Hydroxy*-3-*chloroacetophenone.*—Anhydrous aluminium chloride (30 g.) was added to *o*-chlorophenyl acetate (32.7 g.) in a flask provided with a calcium chloride guard tube, and heated in an oil-bath for 2 hours at 110°. The reaction product was decomposed with HCl (dil.). The crude 2-hydroxy-3-chloroacetophenone was filtered and crystallised from alcohol, m.p. 84°, yield 13 g. (40%). It responds to Pyman's test. (Found: C, 56.01 ; H, 4.02. $C_8H_7O_2Cl$ requires C, 56.31 ; H, 4.11%). Semicarbazone, m.p. 196°.

2-*Hydroxy*-3-*chloropropiophenone.*—The method followed was the same as above. The crude 2-hydroxy-3-chloropropiophenone was crystallised from aqueous alcohol as a yellow solid, m.p. 72°, yield 35%. The compound responds to Pyman's test. (Found: C, 58.12 ; H, 4.32. $C_9H_9O_2Cl$ requires C, 58.53 ; H, 4.88%). Semicarbazone, m.p. 130°.

2-*Hydroxy*-3-*chlorobutyrophenone* was prepared by the usual method, but it was fouud that by increasing the reaction time from 2 to 4 hours, the yield of the *o*-hydroxyketone increased from 17 to 36.5%. Recrystallised from alcohol, it melts at 118° and responds to Pyman's test. (Found: C, 59.92 ; H, 5.12. $C_{10}H_{11}O_2Cl$ requires C, 60.45 ; H, 5.54%). Semicarbazone, m.p. 142°.

Benzofurans.—*o*-Hydroxyketone (1 mole) was added to 1.25 moles of caustic potash dissolved in sufficient ethanol. To this was added phenacyl bromide (1 mole) and the mixture refluxed for 2½ to 4 hours. The alcohol was distilled off and water added to the cooled residue. The crude product was filtered and recrystallised from alcohol (or acetic acid in certain cases).

Oxime & Semicarbazone.—To the benzofuran (0.5 g.), dissolved in sufficient 95% ethanol, were added hydroxylamine hydrochloride (1 g.) and pyridine (1 c.c.), and refluxed for 2 hours. Most of the alcohol was then distilled off, and to the residue water was added gradually to precipitate the oxime. It was filtered, washed with hot water and crystallised from alcohol.

The semicarbazone was prepared likewise using semicarbazide hydrochloride instead of hydroxylamine hydrochloride in the above method.

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Received January, 15, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

COMPOSITION OF CUPRIC *o*-CRESOTATE CHELATES: A COLORIMETRIC STUDY

By S. C. Tripathi and Satya Prakash

Copper^{II} forms chelates with *o*-cresotic acid. In 1 : 1 mixtures of cupric sulphate and monosodium *o*-cresotate, the green colour intensifies on increasing the p_H, and maximum colour is obtained at p_H 5.2. The composition of the complex has been determined at p_H 5.2 and 5.0, which indicates the formation of a green complex containing cupric ion and *o*-cresotate in 1 : 1 ratio.

In 1 : 2 and 1 : 3 mixtures of cupric sulphate and monosodium *o*-cresotate, the colorimeter readings show maximum at p_H 5.7, which indicates the formation of some complex other than 1 : 1. The composition of this complex has also been determined by Job's method at p_H 5.7, and it contains cupric ion and *o*-cresotate in 1 : 2 ratio. In between 5.7 and 5.2, intermediate mixtures of the two complexes exist.

Copper salicylate complexes have been investigated by Babko (*J. Gen. Chem. U.S.S.R.*, 1947, **17**, 443) by Job's method (*Ann. chim.*, 1928, *x*, **9**, 113; Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437). Turner and Anderson (*J. Amer. Chem. Soc.*, 1949, **71**, 912) studied the copper sulphosalicylate complexes spectrophotometrically.

Experimental

Standard solutions of cupric sulphate were prepared by direct weighing of an Analar-B D.H. sample of copper sulphate ($CuSO_4, 5H_2O$) and dissolving it in water. Fresh solutions were always prepared to avoid effects due to hydrolysis.

The monosodium salt of *o*-cresotic acid was prepared as described by Tripathi and Prakash (this *issue*, p. 119). Standard solutions of monosodium *o*-cresotate were prepared by direct weighing of the prepared sample.

All the measurements were made at a constant temperature of 30° ± 0.1°. p_H and colorimetric measurements were made as in the case of complex formation of uranyl ion with *o*-cresotic acid (Tripathi and Prakash, *loc. cit.*).

Complex-forming Systems.—To study the complex formation of copper^{II} with monosodium *o*-cresotate, monovariant method was used as in complex formation of uranyl ion with *o*-cresotic acid (*loc. cit.*).

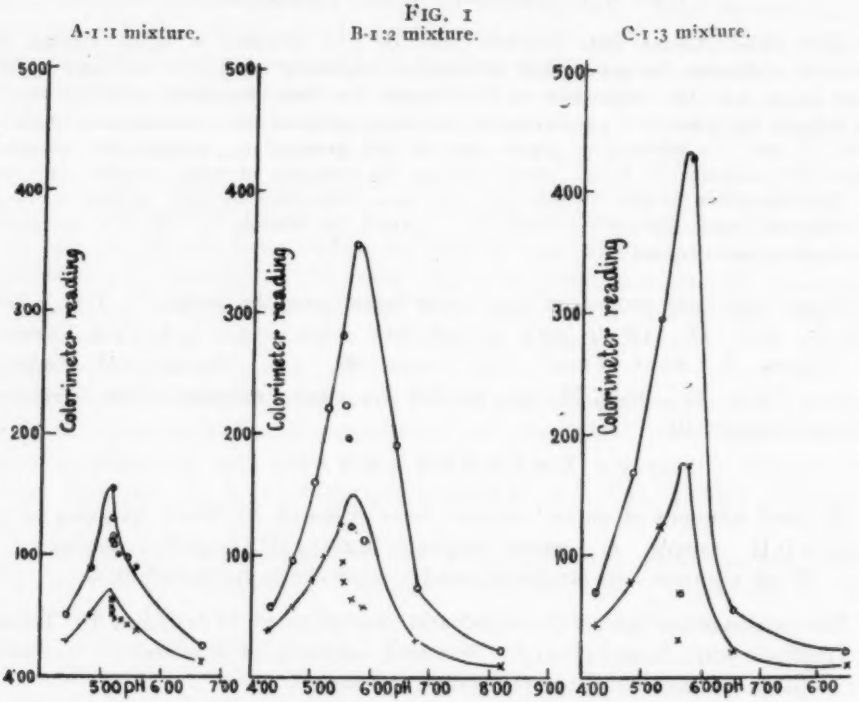
To study Job's method of continuous variation, different mixtures of Cu^{2+} and monosodium *o*-cresotate were prepared in various ratios at constant p_H's of 5.20, 5.0, 5.7 and 5.4. The p_H's of the mixtures were raised by alkali. The total volume of each mixture was kept 50 c.c. The colorimetric measurements of the mixtures were made with filters Ks42 and Ks 47 within the transmission ranges of 400−450 mμ and 455−505 mμ respectively after the attainment of equilibrium.

Discussion

In the graphs the abscissa represents the p_H or the ratio of the concentration of monosodium *o*-cresotate to the total concentration of monosodium *o*-cresotate and cupric ion, while the ordinate represents colorimeter readings.

Fig. 1 shows the changes in colour with the rise in p_H in 1 : 1, 1 : 2 and 1 : 3 mixtures of 0.0667*M* cupric sulphate and 0.0667*M* monosodium *o*-cresotate. Colorimeter readings with filters Ks 42 and Ks 47 have been plotted against p_H.

FIG. 1



The two curves in Fig. 1-A show that increase in colorimeter readings takes place by the addition of alkali up to p_H 5.2 in 1 : 1 mixtures of Cu^{2+} and monosodium *o*-cresotate ; after that precipitation of copper hydroxide starts and is complete at about p_H 8.0. Inference can be drawn from this that a green coloured complex is formed in the systems containing Cu^{II} and *o*-cresotate, most probably in 1 : 1 ratio.

As the maximum in colorimeter readings is at p_H 5.2 (Fig. 1-A) the formation of the complex may be presumed at p_H 5.2, and above this p_H the complex breaks up.

For the determination of the composition of the complex, Job's method (*loc. cit.*) was used ; 0.0667*M* cupric sulphate and 0.0667*M* monosodium *o*-cresotate solutions were mixed in various ratios (0.1 to 1.0) of the concentration of monosodium

o-cresotate to the total concentration of monosodium *o*-cresotate and Cu^{2+} ion. The p_H of each mixture was raised to a constant value of 5.2 by alkali and the total volume was kept at 50 c c. in each case (Fig. 2). From the examination of the two curves A and B (Fig. 2) of two filte s Ks 42 and Ks 47, it is clear that maximum in colorimeter readings lies at the ratio of 0.5, indicating the formation of a green complex in 1 : 1 ratio of cupric sulphate and *o*-cresotate at p_H 5.2.

FIG. 3

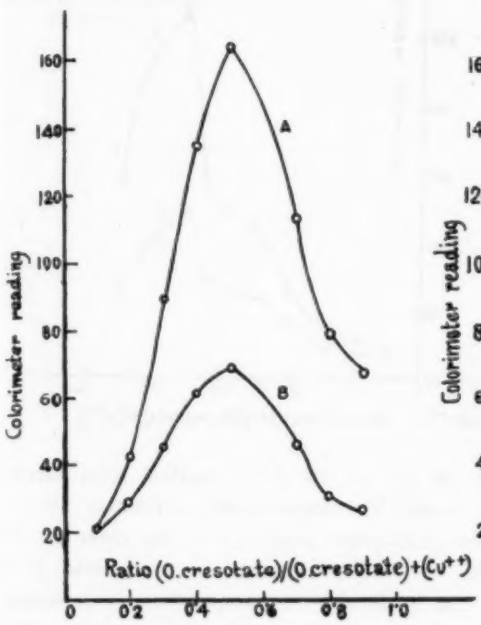


FIG. 2

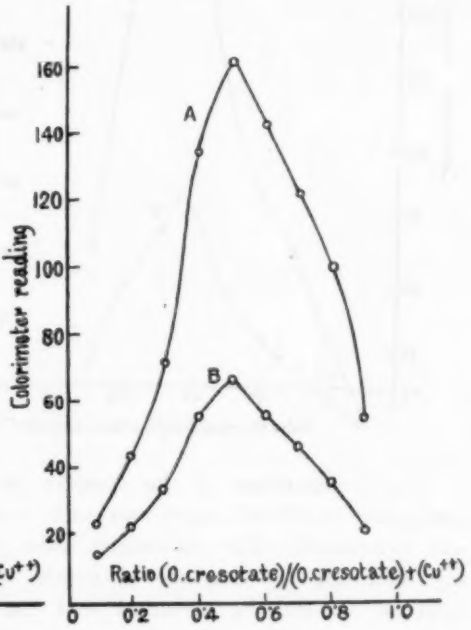
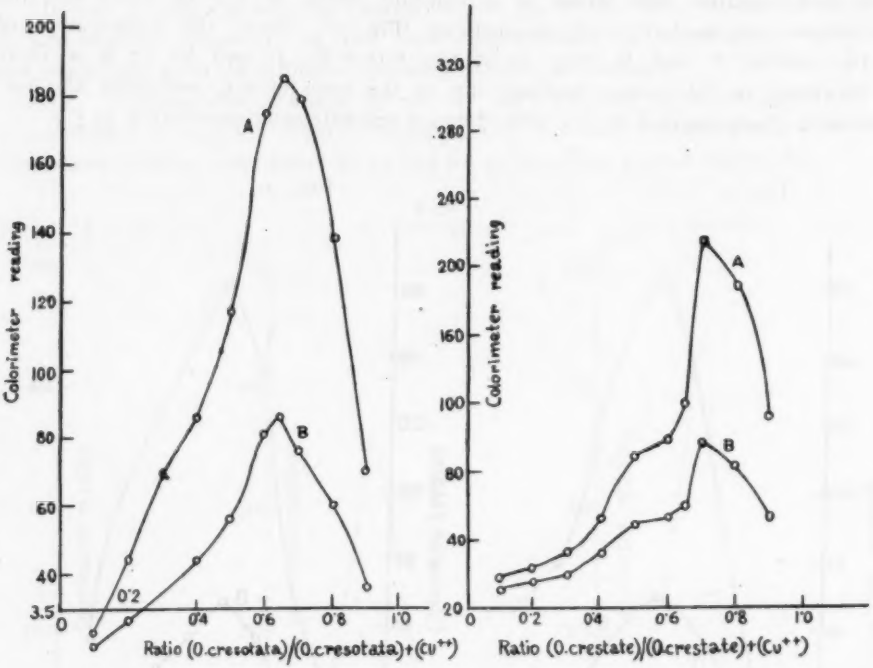


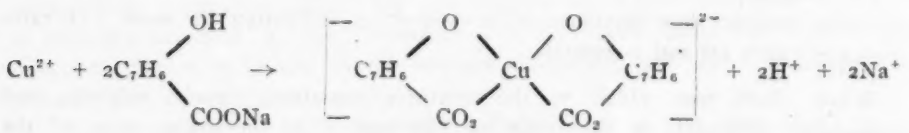
Fig. 3 shows the graphical representation of colorimeter readings of the mixtures containing Cu^{2+} and monosodium *o*-cresotate in various ratios at constant p_H 5.0, keeping the total volume in each mixture constant at 50 c. c. Here also the colorimeter readings show maximum at the ratio of 0.5, indicating the same 1 : 1 ratio complex of cupric ion and *o*-cresotate.

When alkali was added to the mixtures containing cupric sulphate and monosodium *o*-cresotate in the ratios of 1 : 2 and 1 : 3, the green colour of the mixtures deepened (Fig. 1, B, C). The maximum intensity of the green colour in both sets of 1 : 2 and 1 : 3 mixtures was at a somewhat higher p_H than that of 1 : 1 mixture (Fig. 1, A). The colorimeter readings showed maximum at p_H 5.7, indicating the formation of a different complex but not of 1 : 1 ratio. This complex was not stable above p_H 5.7 and cupric hydroxide was precipitated above this p_H.

FIG. 5 FIG. 4



The composition of the complex at p_H 5.7 by Job's method with mixtures containing (0.0667*M*) cupric ion and (0.0667*M*) monosodium *o*-cresotate (Fig. 4) was determined. The colorimeter gave maximum readings at the ratio of about 0.7, indicating the presence of cupric ion and *o*-cresotate in 1 : 2 ratio in the complex. It can be presumed that the hydrogen of monosodium *o*-cresotate is displaced in the complex formation and co-ordination takes place with oxygen atoms of hydroxyl and carboxyl groups. It can be concluded that this 1 : 2 complex is a chelate of the following structure :



The colour maximum of the mixtures of various ratios of cupric ion and monosodium *o*-cresotate at constant p_H of 5.4 is at the ratio of 0.65 (Fig. 5), *i.e.* at p_H 5.4, the intermediate mixtures of both the complexes are present.

It becomes quite clear from the above observations that cupric ions for two green-coloured complexes with monosodium *o*-cresotate. One complex is formed up to p_H 5.2 containing cupric ion and *o*-cresotate in 1 : 1 ratio and the other complex at p_H 5.7 containing cupric ion and *o*-cresotate in 1 : 2 ratio. The 1 : 1 ratio complex breaks up above p_H 5.2 and 1 : 2 ratio complex, above p_H 5.7.

Authors are thankful to the Scientific Research Committee of the U.P. Govt. for the award of a research assistantship to one of them (S.C.T.).

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Received March 7, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

STUDIES ON THE COMPOSITION OF THALLIUM FERROCYANIDE BY PHYSICO-CHEMICAL METHODS

By J. N. Gour, H. C. Gour and Abani K. Bhattacharya

The composition of thallium ferrocyanide has been studied by conductometric, potentiometric and thermometric titrations at several dilutions of the reactants, potassium ferrocyanide and thallium nitrate. The composition of the complex agrees with the formula $Tl_4Fe(CN)_6.2H_2O$.

Flecher and Benzian (*Chem. Zentrl.*, 1902, **26**, 49) observed that a yellow crystailine compound, $Tl_4Fe(CN)_6.2H_2O$ was obtained, when hot concentrated solution of thallous sulphate was added to potassium ferrocyanide solution and the mixture allowed to cool. The crystalline precipitate was sparingly soluble in cold, but more readily in hot water. In order to study the composition of the precipitated compound by physico-chemical methods, conductometric, potentiometric and thermometric titrations were performed at different dilutions and molar concentrations of the reactants. The composition, determined by the above mentioned methods in aqueous and aqueous-alcoholic solutions, has been reported in this paper.

Experimental

Thallium nitrate (Merck's guaranteed reagent) was dissolved in conductivity water, and thallium estimated as Tl_2CrO_4 (Vogel, "Quantitative Inorganic Analysis", p. 564). Potassium ferrocyanide was estimated as described in our previous publication (this *Journal*, 1951, **28**, 473). Determinations of conductivity and the measurement of E.M.F. were carried out as described earlier (*ibid.*, 1953, **30**, 158, 163). The results of the conductometric and thermometric titrations of thallium ferrocyanide are recorded in Table I, and potentiometric measurements in Table II.

Table I

$M/5$-$K_4Fe(CN)_6$ and $M/5$-$TlNO_3$. Conc. ratio (n) = 1 : 1.

†$M/5$-$TlNO_3$ (V).	Alcohol added.	$M/5$-$K_4Fe(CN)_6$ required for V c.c of $M/5$-$TlNO_3$ (V_1 c.c.)	$M/5$-$K_4Fe(CN)_6$ calc. for 10 c.c. of $M/5$-$TlNO_3$ $(V_1/V)\times 10$.	Compound formed.	Curve No.
		Conductometric.			
* 10 c.c.	0 c c.	2 2 c c	2.20 c.c.	$Tl_4Fe(CN)_6$	1
9	1	2.1	2.32	Do	2
8	2	2.0	2.50	Do	3
		Thermometric.			
20	0	4.0	** { 4.0		4
18	2	3.7	** { 4.10		5
16	4	3.4	** { 4.25		6

† For conductometric method $TlNO_3$ was taken in the cell and for thermometric study, in a Dewar flask.

*Calc. titre value for 10 c c. of $M/5$-$TlNO_3$ for the formation of the compound $Tl_4Fe(CN)_6$ is 2.50 c c. of $M/5$-$K_4Fe(CN)_6$

** For 20 c.c. of $M/5$-$TlNO_3$.

TABLE II

$M/5$-$TlNO_3$.	Alcohol added.	Range for maximum change in DE/dc.	Curve No.
20 c.c.	0 c.c.	4.0 to 4.2	7
18	2	3.6 ,, 3.8	8
16	4	3.2 ,, 3.4	9

At the equivalence point the curve did not show a steep fall. The value of DE/dc became maximum in the vicinity of the equivalence point.

FIG. 1

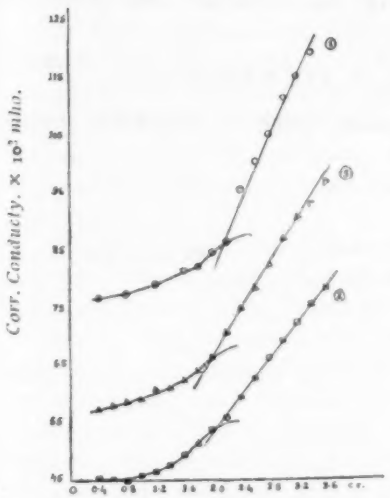
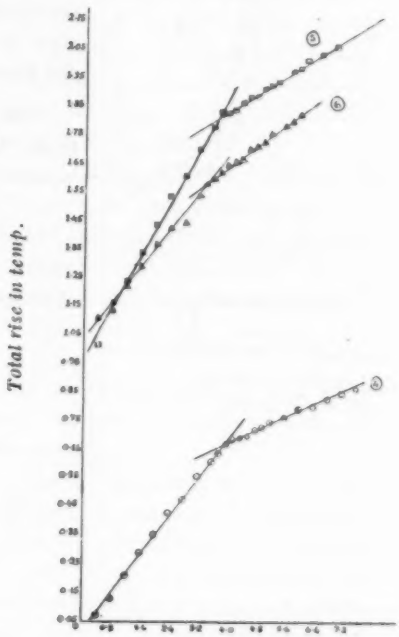


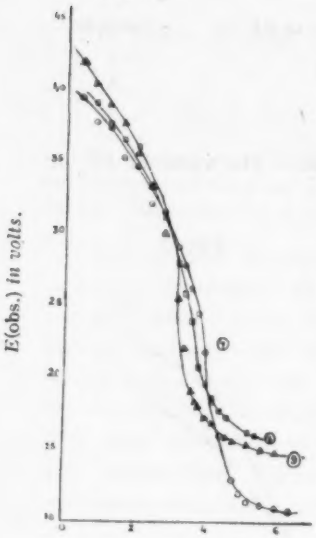
FIG. 2



DISCUSSION

It was observed that the behaviour of thallium ferrocyanide was unlike that of the insoluble complexes of uranyl and thorium ferrocyanides, communicated previously (this *Journal*, 1953, **39**, 159; 1954, **31**, 467). A little or no precipitate was formed when dilute solutions were mixed; the precipitated complex was definitely crystalline. It was partly soluble in excess of water, more in hot than in cold; it could, however, be almost quantitatively precipitated by mixing $M/5$ solutions of the reactants and of higher concentrations. Since the precipitate would dissolve in excess of $K_4Fe(CN)_6$, it was only possible to perform the conductivity titrations by taking the thallium nitrate in the conductivity cell and $K_4Fe(CN)_6$ in the burette.

FIG. 3



When the titrations were carried out in aqueous medium, the observed titre values were slightly less than the calculated equivalent (vide table & curves), but in a queous alcoholic medium the titre approached the equivalent amount ; the formula $Tl_4Fe(CN)_6$ for the precipitate was in agreement with the titre obtained in presence of 20% alcohol by conductometry, and the titre equivalents of thermometric curves were only in fair agre ement with the conductometric result. The potentiometric curves did not show a very steep fall and, hence, more divergence from the theoretical value was observed.

The low values of the titre in aqueous solutions follow from the solubility of the cystalline precipitate. An equilibrium

$$Tl_4Fe(CN)_6 \rightleftharpoons 4Tl^{\cdot} + Fe(CN)^{IV}_6$$

exists near the end-point, which is responsible for the discrepancies observed.

DEPARTMENT OF CHEMISTRY,
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Received May 29, 1957

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

SHORT NOTES

SEARCH FOR NEW INSECTICIDES

By S. S. Tiwari and Brajendra Nath Tripathi

The synthesis of various 2-allyloxy- and 2-*o*-chlorobenzyloxy-4:5-dimethylphenyl alkyl ketones, and of 2-allyloxy-4:6-dimethyl α-furophenone as potent contact insecticides containing allyl or *ortho*-chlorobenzyl groups as toxophore and ether and ketonic linkages as lipoid solubilising groups, has been described previously (this *Journal*, 1954, **31**, 76; 1956, **33**, 214). This communication describes their insecticidal activity in terms of 50% and 100% knock-down of common house-flies.

All these compounds are mildly active. Only 2-*o*-chlorobenzyloxy-4 : 5-dimethyl propiophenone and 2-allyloxy-4 : 6-dimethyl α-furophenone have been found to be more active knock-down compounds as compared to D.D.T. and B.H.C. It appears that the activity of 2-allyloxy-4 : 6-dimethyl α-furophenone owes much to the presence of α-furoyl group rather than to allyloxy group, as many α-furoyl compounds have been reported to be good contact insecticides (Gilman and Hewett, *Iowa State Col. J. Sci.*, 1932, **6**, 439; 1933, **7**, 419).

Bioassay of Insecticidal Action.—The testing of the insecticidal activity has been done exclusively against 5 days old and laboratory-bred common house-flies, obtained from regular test-fly colony reared for biological standardisation.

The various compounds were first diluted in mineral turpentine to 1% (w/v) strength ; 0.2 c.c. of the solutions, so obtained, was sprayed by means of an aero spray gun at a predetermined pressure into glass jars, standing on a revolving table, covered by mosquito netting and containing 20 test-flies per test. Each test was carried in duplicate. The periods required to ensure the dorsal position of 50% and 100% of the flies exposed to the insecticidal spray were recorded. In one instance, when a slow insecticidal activity was noticed, the percentage of knock-down for 60 minutes was recorded. The results given here are the average of the two experiments. In the control experiments, *i.e.* spraying of the flies with solvent alone did not exhibit any mortality within the time of observation.

For the sake of comparison of the insecticidal activity of the compounds with standard insecticides, the results under the same conditions of the experiments have also been recorded with the following:

(*a*) 2 : 2-*bis*-(4′-chlorophenyl)-1.1 : 1-trichloroethane or D.D.T. (1% solution).

(*b*) Hexachloro*cyclo*hexane or B.H.C. (having 13% γ-isomer, 1% solution).

(*c*) Pyrethrin I & II (0.02% solution).

During the testing time the temperature remained 28° to 30° and the relative humidity 76% to 83%.

TABLE I

[A= 2-Allyloxy-4 : 5-dimethyl-. B= 2-*o*-Chlorobenzyloxy-4 : 5-dimethyl-].

No.	Compound.	Knock down. 50%.	100%.	No.	Compound.	Knock down. 50%	100%
1.	A acetophenone	30.5 min	45.0 min	9.	B-butyrophenone	16.5	37.5
2.	A-propiophenone	43 5	60.0	10.	B-caprophenone	11.5	19 5
3.	A-butyrophenone	27.0	45·5	11.	B-heptophenone	21.0	53·5
4.	A-caprophenone	16.0	22.0	12.	B-caprylophenone	16.5	47·5
5.	A-heptophenone	19.0	33·5	13.	2-Allyloxy-4 :6'-dimethyl-ferophenone	3 5	9.0
6.	A-caprylophenone	13.0	24·5		D.D.T.	5·5	9·5
7.	B-acetophenone	40% K' D in bomins.			B.H.C.	5.0	7.0
8.	B-propiophenone	3 0	7·5		Pyrethrin I & II	14.3	34·3

The authors are grateful to Geigy Insecticides Limited, Bombay-1 for assaying the insecticidal activity of the compounds described in this paper and to Dr. A. B. Sen for his interest in the work.

THE CHEMICAL LABORATORIES,
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Received October 17, 1957.

[Jour. Indian Chem. Soc., Vol. 35, No. 2, 1958]

ON THE REACTION OF DIETHYLAMINE WITH A SATURATED AQUEOUS SOLUTION OF ANTIMONY TRICHLORIDE

BY S. MOHAPATRA AND CH. B. NANDA

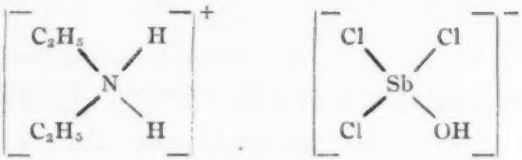
Secondary amines have got very little tendency to function as a donor molecule. It was therefore thought worthwhile to study the reaction of an aliphatic secondary amine with a saturated aqueous solution of antimony trichloride. The results of the investigation with diethylamine are recorded herein.

Pure chemicals were used. A saturated aqueous solution of antimony trichloride was cooled in ice and an ice-cold sample of diethylamine was added dropwise with stirring. The addition of an excess of the latter reagent was avoided. Much heat was produced and a white solid was obtained. It was filtered through a sintered glass crucible and repeatedly washed with ether till free from antimony trichloride. It was dried in vacuum over concentrated sulphuric acid for over 72 hours.

Like the compound obtained with dioxan (this *Journal*, 1956, **33**, 532) it is easily hydrolysed by water and an aqueous extract gives the test of antimony. It is soluble in hydrochloric acid and reacts with a solution of sodium hydroxide affording a clear solution and ammonia. It melts at 90° with decomposition and liberation of ammonia.

Analysis.—Antimony, chlorine and nitrogen contents were estimated as done in the pyridine compound (this *Journal*, 1956, **33**, 538). The mean value of four different samples analysed are: Sb 38.40%, chlorine 33 80%, and nitrogen 4.54% and those calculated for $(C_2H_5)_2NH.SbCl_3.H_2O$ are 38.15%, 33.35% and 4.38% respectively. The corresponding amount of diethylamine calculated from the nitrogen content is 22.84%. If water content is taken as the difference of the sum of the percentages of Sb, Cl and $(C_2H_5)_2NH$ from hundred, it comes out to be 5.66% (calculated for the above compound is 5.63%).

The compound is most probably a salt of the type obtained with dioxan (*loc. cit.*, p. 532) and may be represented by



The authors are thankful to Dr. S. Pani, Reader in Chemistry, University College of Engineering, Burla for his interest in this work.

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2.	Periodicity of its publication	... Monthly
3.	Printer's Name	... Sri Sibendranath Kanjilal
	Nationality	... Indian
	Address	... Calcutta University Press, 48, Hazra Road, Ballygunge, Calcutta.
4.	Publisher's Name	... G. Banerjee, Esq., M.Sc.
	Nationality	Indian
	Address	... Indian Chemical Society, 92, Upper Circular Road, Calcutta-9.
5.	Editor's Names	... (1) Dr. R. C. Shah, D.Sc., F.N.I. (2) Prof. S. R. Palit, D.Sc., F.R.I.C., F.N.I.
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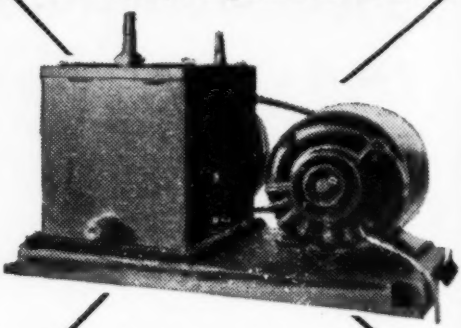

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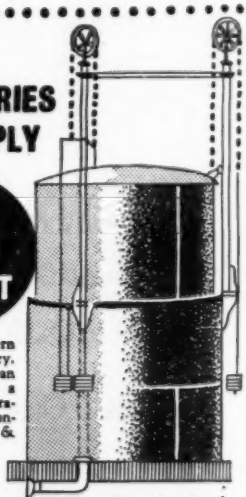

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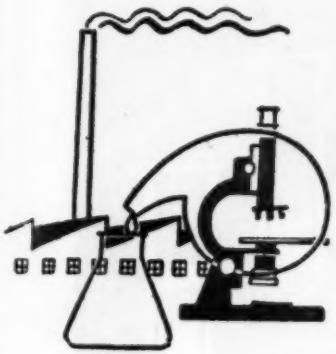

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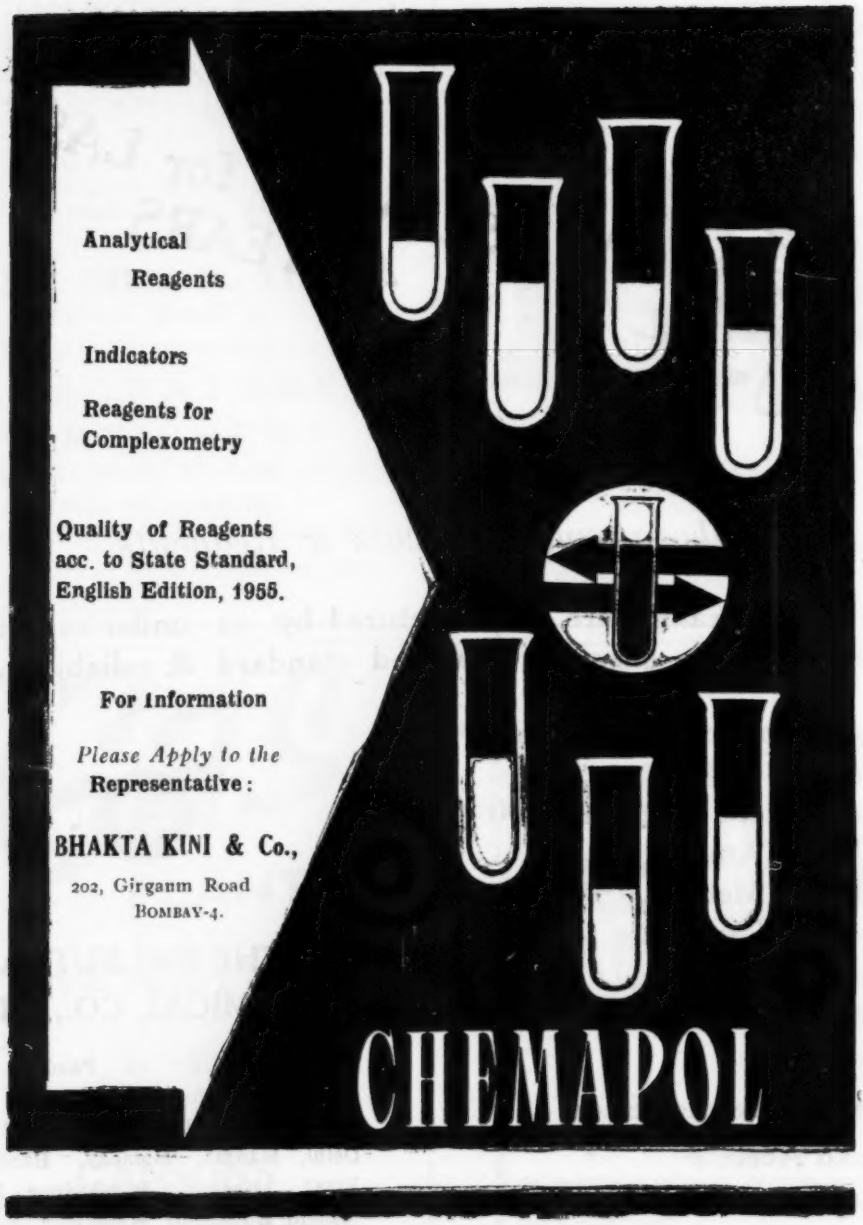

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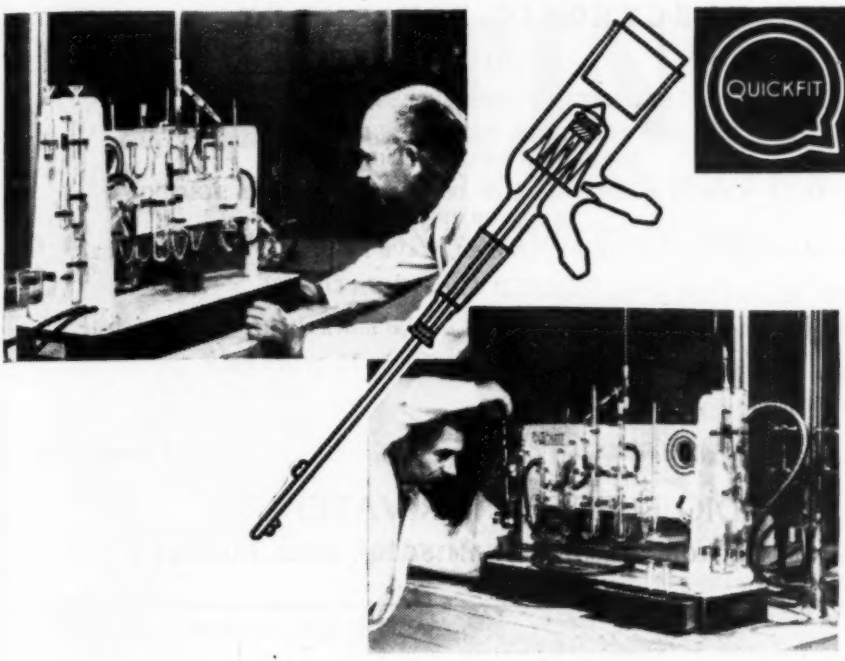

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Printed by Sri Sibendranath Kanjilal, Superintendent, Calcutta University Press., 48, Hazra Road., Ballygunge, Calcutta and Published by G. Banerjee, Esq., M.Sc., Asst. Editor., Indian Chemical Society.